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ENVIRONMENTAL IMPACT GUIDELINES FOR NEW SOURCE NON-FERTILIZER PHOSPHATE MANUFACTURING FACILITIES

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Preface

This document is one of a series of industry-specific Environmental Impact Guidelines being developed by the Office of Federal Activities (OFA) for use in EPA's Environmental Impact Statement preparation program for new source NPDES permits. It is to be used in conjunction with Environmental Impact Assessment Guidelines for Selected New Source Industries, an OFA publication that includes a description of impacts common to most industrial sources.

The requirement for Federal agencies to assess the environmental impacts of their proposed actions is included in Section 102 of the National Environmental Policy Act of 1969 (NEPA), as amended. The stipulation that EPA's issuance of a new source NPDES permit as an action subject to NEPA is in Section 511(c)(1) of the Clean Water Act of 1977. EPA's regulations for preparation of Environmental Impact Statements are in Part 6 of Title 40 of the Code of Federal Regulations; new source requirements are in Subpart F of that Part.

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GLOSSARY

Adiabatic - A process in which no heat is transferred between the system and its surroundings.

Apatite - A natural calcium phosphate usually containing fluorine which occurs as phosphate rock.

Barn - A room-like condensation chamber for anhydrous phosphorus pentoxide.

Burden - The combined rock, coke, and silica feed to a phosphorus electric furnace.

Calcination - Heating of a solid to a temperature below its melting point to bring about a state of thermal decomposition or a phase transition other than melting.

Calcium phosphates - Dicalcium - $CaHPO_4 2H_2O$ or $CaHPO_4$; Monocalcium - $CaH_4(PO_4)_2$ H_2O or $CaH_4(PO_4)_2$; Tricalcium - $Ca_3(PO_4)H_2$ Mole ratio of CaO to P_2O_5 3 to 1.

DCP - Dicalcium Phosphate Dihydrate ($CaHP_4H_2O$).

Defluorinated phosphate rock - Apatite rock which has been treated to remove fluorides. It contains 30 weight percent P_2O_5, 0.2 weight percent fluoride.

Dry Process Phosphoric Acid - Phosphoric acid made from elemental phosphorus; also called furnace acid.

Eutectic - The lowest or highest melting point of an alloy or solution of two or more substances that is comprised of the same components.

Ferrophosphorus - A by-product iron-phosphorus alloy of phosphorus smelting, typically containing 59 percent iron and 22 percent phosphorus.

Flux - A substance that promotes the fusing of minerals or metals or prevents the formation of oxides. For example, in metal refining lime is added to the furnace charge to absorb mineral impurities in the metal. A slag is formed which floats on the bath and is run off.

Furnace Acid - Phosphoric acid made from elemental phosphorus. Also called dry process phosphoric acid.

Gangue - The minerals and rock mined with a metallic ore but valueless in themselves or used only as a by-product.

Gyp-pond - This term is widely used at fertilizer phosphate plants to indicate the pond receiving wastewater and acting as a recirculation, cooling, and water reuse pond. Many plants have ponds with a variety of functions such as receiving the calcium sulfate residue from acid treatment of rock, receiving calcium fluoride from first stage of lime precipitation, receiving calcium phosphate and calcium fluoride sediment from second stage of lime precipitation, recirculation of stack washing and tail gas scrubber water and simultaneously removing heat and sediment, and deposition of troublesome

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solids, as arsenic sulfide. Local authorities will have to determine specific pond uses in order to establish essential solid waste control and groundwater pollution control measures.

Hydrolysis - A chemical reaction in which water reacts with another substance to form one or more new substances.

Immiscible - The property of one liquid being unable to mix or blend uniformly with another.

l - liter.

Nodule - Semi-fused agglomerated and calcined phosphate rock particle.

Phossy water - Water from the phosphorus condenser or phosphorus storage that is contaminated with colloidal phosphorus, fluosilicates, and dissolved solids.

Phosphorus mud - Sludge or emulsion of phosphorus, dust, and water.

Phosphorus Oxychloride - $POCl_3$

Phosphorus Pentasulfide - P_2S_5

Phosphorus Pentoxide - P_2O_5

Process water - Any water which, during the manufacturing process, comes into direct contact with any raw material, intermediate, product, by-product, or gas or liquid that has accumulated such constituents.

Slag - The fused agglomerate which separates in metal smelting and floats on the surface of the molten metal. Formed by combination of flux with gangue of ore, ash or fuel, and perhaps furnace lining. The slag is often the medium by means of which impurities may be separated from metal, or in this case phosphorus.

Soda ash - Soda ash is the source of sodium in sodium phosphate and sodium polyphosphate plants. Commercial grade contains 99 weight percent Na_2CO_3.

Sodium Phosphates - Sodium orthophosphates

Orthodisodium - NaH_2HPOH_4
Orthomonosodium - NaH_2PO_4
Orthotrisodium - Na_3PO_4
Viteous sodium 63-66 weight percent P_2O_5; 34-37 weight percent Na_2O.

Sodium poly (pyro) phosphates

Sodium acid pyro - $Na_2H_2P_2O_7$
Tetrasodium pyro - $Na_4P_2O_7$
Sodium tripoly - $Na_5P_3O_{10}$

Sump - A pit or reservoir serving as a receptacle for condensed phosphorus.

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Welfare-related Pollutants - Pollutants for which adverse effects on human health have not been demonstrated but which exhibit environmental effects.

Wet Process Phosphoric Acid - Phosphoric acid made from phosphate rock and sulfuric acid.

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INTRODUCTION

The Clean Water Act requires that the United States Environmental Protection Agency (USEPA) establish standards of performance for categories of new source industrial wastewater dischargers. Before the discharge of any pollutant to the navigable waters of the United States from a new source in an industrial category for which performance standards have been proposed, a new source National Pollutant Discharge Elimination System (NPDES) permit must be obtained from either USEPA or the state (whichever is the administering authority for the state in which the discharge is proposed). The Clean Water Act also requires that the issuance of a permit by USEPA for a new source discharge be subject to the National Environmental Policy Act (NEPA), which may require preparation of an Environmental Impact Statement (EIS) on the new source. The procedure established by USEPA regulations (40 CFR 6 Subpart F) for applying NEPA to the issuance of new source NPDES permits may require preparation of an Environmental Information Document (EID) by the permit applicant. Each EID is submitted to USEPA and reviewed to determine if there are potentially significant effects on the quality of the human environment resulting from construction and operation of the new source. If there are, USEPA publishes an EIS on the action of issuing the permit.

The purpose of these guidelines is to provide industry-specific guidance to USEPA personnel responsible for determining the scope and content of EIS's and for reviewing them after submission to USEPA. It is to serve as supplementary information to the previously published document, Environmental Impact Assessment Guidelines for Selected New Source Industries (USEPA 1975), which includes the general format for an EID and those impact assessment considerations common to all or most industries. Both that document and these guidelines should be used for development of an EID for a new source non-fertilizer phosphate manufacturing facility.

These guidelines provide the reader with an indication of the nature of the potential impacts on the environment in the vicinity of the facility and the surrounding region from construction and operation of non-fertilizer phosphate manufacturing facilities. In this capacity, the volume is intended to assist USEPA personnel in the identification of those impact areas that

should be addressed in an EID. In addition, the guidelines present (in Chapter 1.0) a description of the industry; its principal processes; significant environmental problems; and recent trends in location, raw materials processes, pollution control, and environmental impacts. This "Overview of the Industry" is included to familiarize USEPA staff with existing conditions in the industry.

Although this document may be transmitted to an applicant for informational purposes, it should not be construed as representing the procedural requirements for obtaining an NPDES permit or as representing the applicant's total responsibilities relating to the new source EIS program. In addition, the content of an EID for a specific new source application is determined by USEPA in accordance with Section 6.604(b) of Title 40 of the Code of Federal Regulations and this document does not supersede any directive received by the applicant from USEPA's official responsible for implementing that regulation.

These Guidelines are divided into five chapters. Chapter 1.0 is the "Overview of the Industry," described above. Chapter 2.0, "Impact Identification," discusses process-related wastes and the impacts that may occur during construction and operation of the facility. Chapter 3.0, "Pollution Control Technology," summarizes the technology for controlling environmental impacts. Chapter 4.0, "Evaluation of Alternative," summarizes possible alternatives to the proposed action and discusses their evaluation. Chapter 5.0 is a list of references which are useful for additional or more detailed information.

The principal sources used in the preparation of this guidelines document were the Development Document for Proposed Effluent Limitations Guidelines and New Source Performance Standards for the Phosphorus-Derived Chemicals Segment of the Phosphate Manufacturing Point Source Category (USEPA 1973) and the Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Other Non-Fertilizer Phosphate Chemicals Segment of the Phosphate Manufacturing Point Source Category (USEPA 1976). These development documents present evaluations of the industry intended to identify appropriate control levels for water-borne pollutants as a basis for establishing effluent limitations. They present a great deal of information on the industry including process information and information on air emission

controls and solid waste generation as they relate to contamination of liquid wastes. These two documents are recommended as additional sources of information on the Non-Fertilizer Phosphate Industry and may be obtained from the Effluent Guidelines Division of USEPA.

1.0 OVERVIEW OF THE INDUSTRY

Phosphorus, an essential nutrient for both plants and animals, also has numerous uses in the manufacture of industrial chemicals. Phosphate or phosphorus-based chemicals are produced for use in agricultural fertilizers, animal food supplements, human food supplements, metallurgical alloying materials, detergents, lubricating oils, and a variety of other uses. The phosphate industry can be divided into two major groups of related industries based on their products: non-fertilizer and fertilizer phosphate. This document deals with the group of industries producing elemental phosphorus, phosphorus-derived chemicals, and other non-fertilizer phosphate chemicals. Collectively these will be referred to as the non-fertilizer phosphate industry. The phosphate fertilizer industry, by far the larger of the two groups, is the subject of a companion document, Environmental Impact Guidelines for New Source Phosphate Fertilizer Manufacturing Facilities.

The products of the non-fertilizer phosphate industry fall into two distinctive categories: 1) elemental phosphorus and phosphorus-derived chemicals, and 2) other non-fertilizer phosphate chemicals which are derived primarily from fertilizer industry intermediates. These two categories are included under Standard Industrial Classifications (SIC) 2819 (Industrial Inorganic Chemicals) and 2874 (Phosphatic Fertilizers) respectively.

The non-fertilizer phosphate industry is difficult to characterize because its designation is based on the non-fertilizer use of its products rather than on a similarity between its industrial processes and the facilities required for the products' manufacture. This designation is further obscured by the close association between producers of fertilizer and non-fertilizer phosphate chemicals. In general, companies producing non-fertilizer phosphate chemicals are large, integrated chemical or petrochemical companies with diversified interests throughout the chemical industry (USEPA 1973b, USEPA 1974b). Most of these companies also have interests in the fertilizer industry and produce both fertilizer and non-fertilizer products. Many of the plants producing non-fertilizer phosphate products are part of large integrated chemical complexes which produce a wide variety of both fertilizer and non-fertilizer phosphate chemicals while others are small operations producing

only one or two products which are shipped to other plants for further processing.

It is not uncommon for one company to be involved in all aspects of the industry from ore extraction to production of finished products. Because economics dictate that processing facilities which utilize bulky phosphate rock be near their source of raw materials, it also is common for a company to have several operations in the mining area or even on one site (USEPA 1973a). For example, a plant located at or near a phosphate rock mine site may be involved in mining and preparing the rock, as well as producing a variety of phosphate and non-phosphate fertilizer products and non-fertilizer phosphate products on the same or nearby sites. The non-fertilizer phosphate production at such a facility may be a small part of a much larger operation and, consequently, the impacts of this operation may be difficult to distinguish from those of other operations.

Due to the degree of integration and diversification among the companies producing phosphate chemicals, it is necessary to view the non-fertilizer phosphate industry in context with the related mining and fertilizer industries. Not only are the industries related in terms of raw materials, processes, and facilities, but they also may be located in close proximity to each other and share common environmental problems. The major mining and manufacturing operations related to production of phosphate chemicals and fertilizer are briefly described in the following paragraphs to highlight the interrelationships and distinctions among the various segments of the non-fertilizer phosphate industry (USEPA 1980).

- Phosphate mining industry. This is a segment of the mining industry which extracts phosphate ores and processes them to produce marketable quality "phosphate rock." Most ores are sedimentary deposits of the mineral fluorapatite and associated impurities, along with clays, sands, or other rock matrix. These constituents usually must be separated to concentrate the phosphate-bearing deposits which are referred to as "phosphate rock," "phosrock," "phosphate rock concentrate," and "beneficiated phosphate rock."

- Phosphate fertilizer industry. This industry uses phosphate rock from the phosphate mining processes to manufacture phosphate fertilizer chemicals.

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- Non-phosphate fertilizer industries. In reference to the phosphate fertilizer industry, these industries include the "nitrogen" or "nitrogenous" fertilizer industry and the "potassium" or "potash" fertilizer industry. The products of the nitrogen and potash fertilizer industries are usually considered "intermediate," to be combined with other materials or processed further for specific applications.

- Mixed (and blended) fertilizer industry. This is the industry which actually produces most of the fertilizer materials commercially marketed. Phosphate, nitrogen, and potassium fertilizer chemicals, along with various fillers, coating agents, insecticides, and other useful additives, are combined by this industry to produce popular blends or formulations tailored to the needs of certain geographic areas.

- Non-fertilizer phosphate industry. This category includes industries involved in the manufacture of phosphorus-derived and non-fertilizer phosphate chemicals that are widely used for purposes other than soil fertilization. This broad industry category includes the production of phosphorus and ferrophosphorus by smelting phosphate ore; production of phosphoric acid, phosphorus pentoxide, phosphorus trichloride, and phosphorus oxychloride directly from elemental phosphorus; production of sodium tripolyphosphate and animal feed grade and human food grade calcium phosphate from phosphoric acid; defluorination of phosphate rock by high temperature and other treatments; defluorination of phosphoric acid; and purification of sodium phosphates from "wet process" phosphoric acid. These products are used in applications such as human food additives, animal feed supplements, plastics manufacture, metal treatment, detergent builders, and incendiary chemicals.

Where required to enhance the understanding of the non-fertilizer phosphate industry, the interrelationships of the above industry segments are indicated in this document. In general, however, these Guidelines do not address the other industry segments.

1.1 SUBCATEGORIZATION

The non-fertilizer phosphate industry is difficult to identify and subcategorize because its various segments are grouped together as much on the basis of their lack of association with the fertilizer industry rather than on the internal similarity between them.

The industry is generally divided into two categories: 1) elemental phosphorus and phosphorus-derived chemicals, and 2) other non-fertilizer

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phosphate chemicals. Within these general categories, subcategories may be identified by grouping particular manufacturing operations according to their raw materials, products, processes, waste materials, and environmental problems. The industry has been subcategorized by USEPA according to these criteria for the purpose of establishing effluent limitations guidelines and standards pursuant to Section 304 of the Federal Water Pollution Control Act. These subcategories are identified in Table 1 and will be used as the basis for industry descriptions in this document.

Of the six subcategories, only phosphorus production and defluorinated phosphate rock operations are likely to be found as completely separate facilities. The others probably would be found associated with a larger industrial complex manufacturing several products. The degree of integration and diversification among the phosphate manufacturing facilities often makes it difficult to identify the subcategory to which a specific facility may belong. Any new source facility should be examined carefully to determine the subcategory or subcategories within which its manufacturing processes belong.

1.2 PROCESSES

1.2.1 Major Processes of the Non-Fertilizer Phosphate Industry

The major industrial processes of the non-fertilizer phosphate industry include those for the production and use of elemental phosphorus and those for the production of non-fertilizer products from phosphate rock and "wet process" phosphoric acid. The general product manufacturing scheme for the industry is depicted in Figure 1. The initial process for the production of phosphorus and phosphorus-derived chemicals is the production of elemental phosphorus by thermal reduction of phosphate rock in an electric arc furnace (USEPA 1973a). Ferrophosphorus, commonly used in the metallurgical industry, is a direct by-product of this phosphorus production process. Most of the elemental phosphorus produced in this country is used to produce "dry process" or "furnace grade" phosphoric acid. The remainder of the phosphorus either is sold or used to produce chemicals such as phosphorus pentoxide, phosphorus pentasulfide, phosphorus trichloride and phosphorus oxychloride. The "dry process" phosphoric acid produced from phosphorus is of a much higher quality

Table 1. Subcategories of the non-fertilizer phosphate industry.

A. Phosphorus Production facilities manufacture elemental phosphorus from phosphate rock by thermal reduction of the rock with coke and silica in an electric arc furnace.

B. Phosphorus Consuming facilities manufacture chemicals including "dry process" phosphoric acid, phosphorus pentoxide, phosphorus trichloride, phosphorus oxychloride, phosphorus pentasulfide, red phosphorus, and various munitions from elemental phosphorus.

C. Phosphates facilities manufacture high quality phosphate products such as sodium tripolyphosphate and food grade calcium phosphates from "dry process" phosphoric acid.

D. Defluorinated Phosphate Rock facilities chemically or thermally remove fluorine from phosphate rock for production of animal grade phosphate food supplements.

E. Defluorinated Phosphoric Acid facilities remove fluorine from "wet process" phosphoric acid (a major intermediate of the fertilizer industry) for use in the production of animal food grade calcium phosphates and other chemicals.

F. Sodium Phosphates facilities produce high quality sodium phosphate chemicals from "wet process" phosphoric acid (a major intermediate of the fertilizer industry) rather than "dry process" phosphoric acid as done in subcategory B.

Sources: US Environmental Protection Agency. 1973a. Development document for proposed effluent limitations guidelines and new source performance standards for the phosphorus derived chemicals segment of the phosphate manufacturing point source category. Office of Air and Water Programs, Washington DC, 159 p.

US Environmental Protection Agency. 1976a. Development document for effluent limitations guidelines and new source performance standards for the other non-fertilizer phosphate chemicals segment of the phosphates manufacturing point source category. Office of Water and Hazardous Materials, Washington DC, 105 p.

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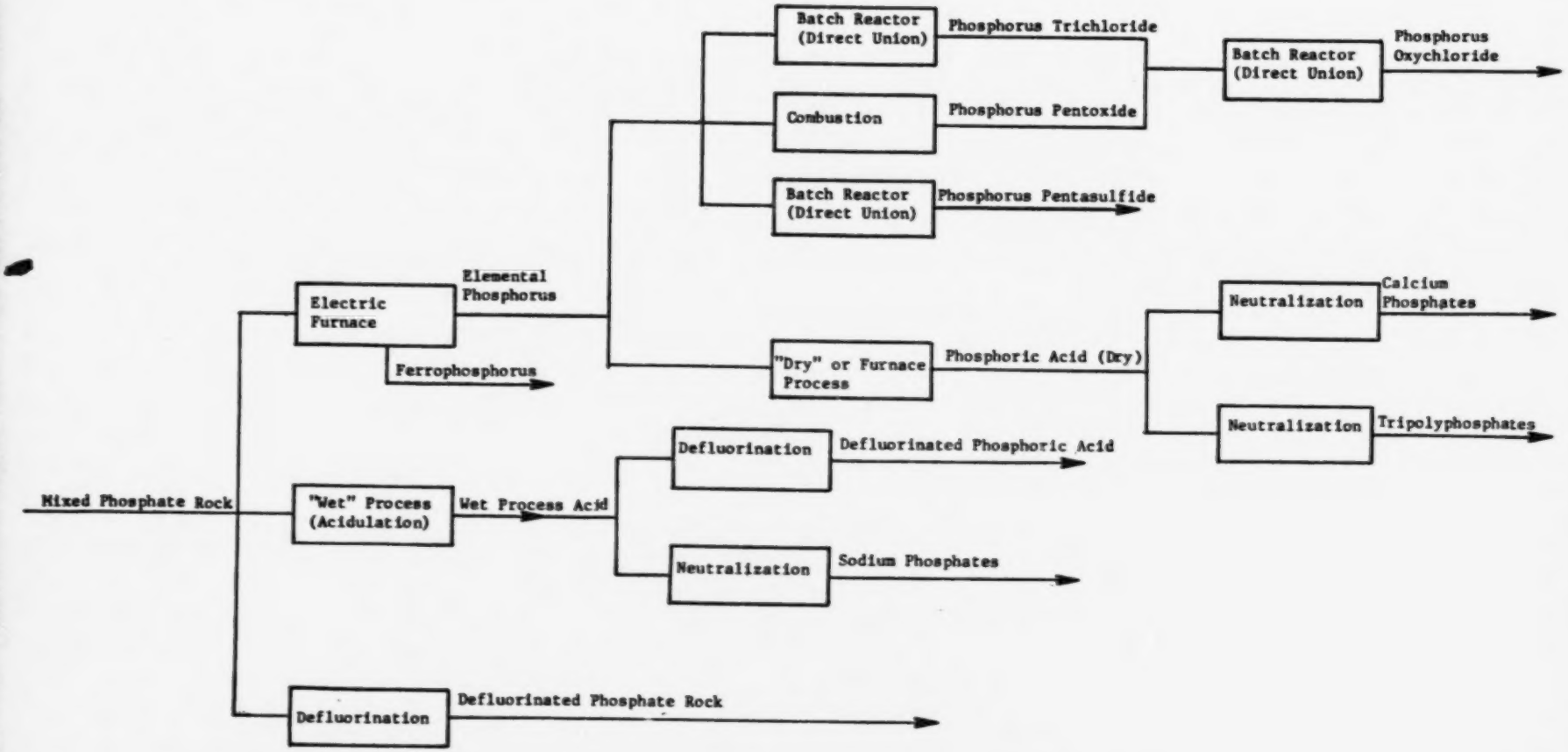
Figure 1. Overall material and product flow diagram for the non-fertilizer phosphate industry.



Source: US Environmental Protection Agency. 1977b. Federal guidelines - state and local pretreatment programs, Appendix 8, Volume III. Office of Water Program Operations, Washington DC, 475 p.

than the "wet process" phosphoric acid of the fertilizer industry and is used largely by the food industry. Products made from "dry process" phosphoric acid include animal and human food grade calcium phosphate, reagent grade phosphate compounds, and sodium tripolyphosphate which is used in detergents and water purification systems.

There is also a demand for phosphate products of adequate quality for soap and animal feed but at a lower cost than those produced from "dry process" acid. These products can be produced from lower grade phosphate materials such as defluorinated phosphate rock and "wet process" phosphoric acid by using appropriate purifying techniques. Defluorinated phosphate rock produced by chemical and heat treatment of phosphate rock is utilized as an animal feed ingredient. Phosphoric acid is defluorinated by evaporation or stripping techniques and is mainly used in the production of animal feeds and some high analysis and liquid fertilizers. With the use of appropriate purification steps, sodium phosphates can be produced from "wet process" acid and used as intermediates in the production of soaps and detergents (USEPA 1976a). These process descriptions are adopted from the development document for effluent guidelines limitations and standards for the Industry (USEPA 1973a and 1976a) unless otherwise noted. Following are general descriptions of the processes used to manufacture non-fertilizer phosphate products.

1.2.1.1 Phosphorus Production (Subcategory A)

Elemental phosphorus is manufactured by the thermal reduction of phosphate rock with reducing carbon (coke) in an electric furnace. Silica in the form of sand is used as a flux. As shown in Figure 2, the standard process for phosphorus production consists of three major subprocesses: furnace charge preparation, thermal reduction in the electric furnace, and product recovery.

Furnace Charge Preparation

The phosphate rock or phosphate rock concentrate used for manufacturing phosphorus is usually conditioned by an agglomeration process in order to obtain a relatively porous furnace burden that will be retained in the furnace

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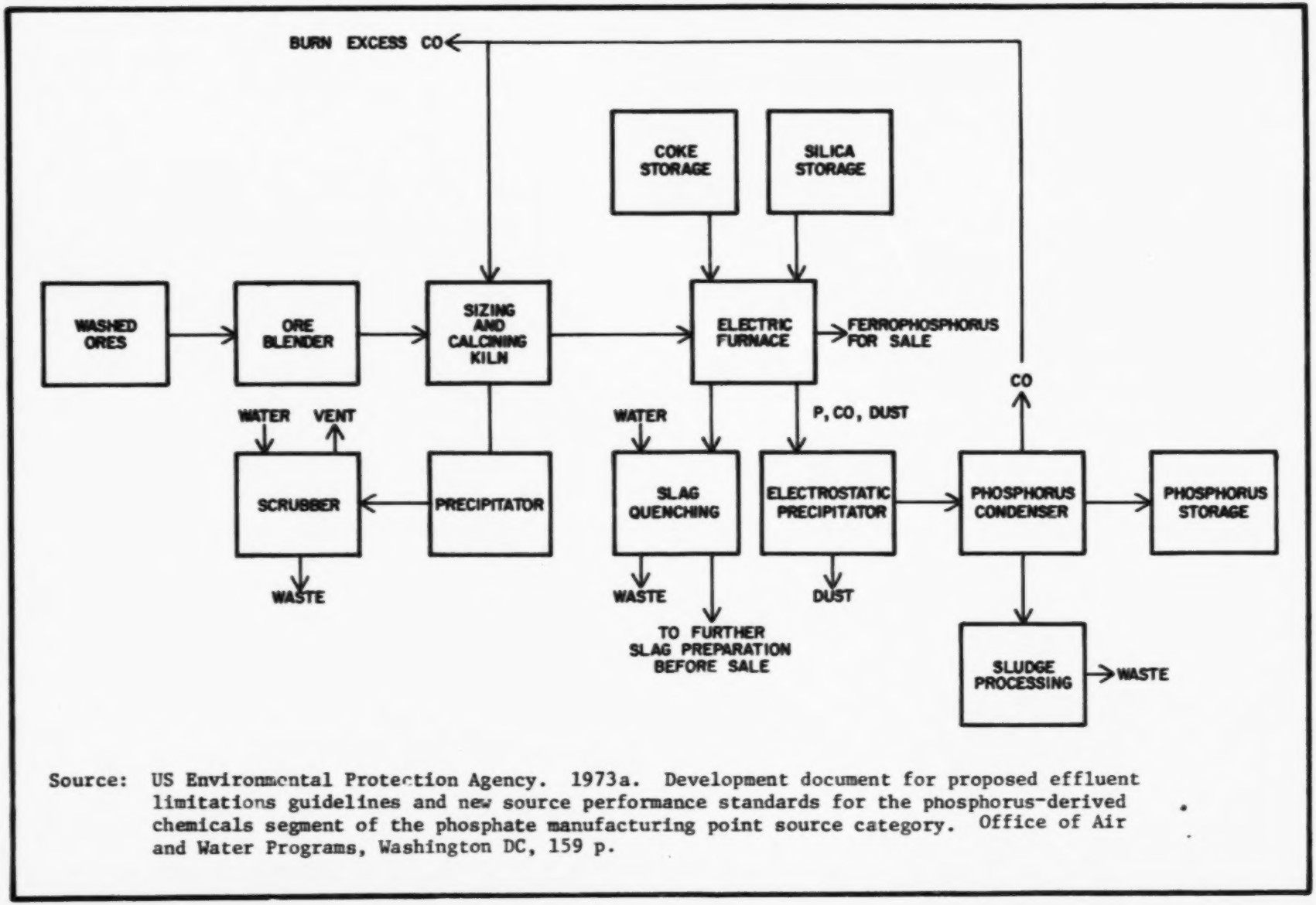
Figure 2. Standard process for production of elemental phosphorus.



Source: US Environmental Protection Agency. 1973a. Development document for proposed effluent limitations guidelines and new source performance standards for the phosphorus-derived chemicals segment of the phosphate manufacturing point source category. Office of Air and Water Programs, Washington DC, 159 p.

during puffs and blows. An agglomerated burden allows reaction gases to escape from the furnace as it is being smelted and promotes more efficient heat transfer throughout the furnace.

Relatively low grade phosphate rock such as that from western states may contain high concentrations of clay or organic material and low concentrations of phosphate reducing its value as a fertilizer material. However, this low grade rock may be used to manufacture elemental phosphorus and phosphate chemicals if properly conditioned.

Commonly used conditioning processes include nodulizing, pelletizing, briquetting and compacting. Sintering may be used at a few existing furnaces but probably would not be used at a new facility. Following pelletizing, briquetting or compacting, the agglomerated burden may need to be calcined to impart the necessary strength. Conditioning processes are described as follows:

- Sintering is an operation in which fine ore is mixed with coke or coal and burned on a moving grate under a strong draft. Heat from the burning coke or coal fuses the phosphatic material into a uniform mass. The sintered ore mixture is then crushed and screened for calcining and smelting. Undersized particles are returned for reprocessing. This process in now considered to be outmoded and probably would not be used at a new source facility.

- Nodulizing involves heat fusing phosphate fines in a rotary kiln. Tumbling in the kiln causes the material to cohere and form rounded nodules suitable for smelting. Feed may be either relatively dry or a wet slurry. The feed may be mixed using pug mixers; crane-bucket mixing; pile building, blending, and reclaiming chaser mills; or layering on conveyor belts. Processing includes rotary drying (dry kiln), cooling of the kiln product (inclined grate cooler), crushing, and screening. Mud rings which form on kiln walls near the discharge end must be removed periodically with a boring bar.

- Pelletizing involves grinding the phosphate to provide a large surface area, adjusting the liquid phase by addition of water and tumbling the material in a drum or pan. Agglomerates are held together by surface tension forces. When the phosphate contains clay, grinding may be unnecessary (Barber 1980b).

- Briquetting involves plasticizing the mixture in an intensive mixture followed by pressure molding into various shapes called briquets. Optimum moisture for briquetting is provided by adding water to par-

tially dried material. Usually clay present in low-grade phosphates serves as a binder for briquetting, but when insufficient clay is present a binder must be added (Barber 1980b).

- Compacting is similar to briquetting except that pressure is exerted on the material by smooth rolls forming a sheet of material of the desired thickness. The sheet of material is broken into chunks of the desired size. Clay serves as the binder, although solids may be agglomerated without a binder if high pressures are exerted by the rolls (Barber 1980b).

- Calcining involves the drying and screening of pellets, briquettes, or sheets and burning them in a rotary kiln just below the fusion temperature to strengthen them. Equipment used for this process includes drums, rotary driers, screens, and rotary kilns.

Thermal Reduction in the Electric Furnace

The prepared furnace burden is charged to a specially designed electric arc furnace along with coke, the reducing agent, and sand, which serves as a flux. Weighed quantities of each material are blended and intermittently fed into the furnace by means of a common conveyor. Phosphate reduction in the arc furnace requires tremendous energy input totaling 13,000 $\pm$ 1,000 kwh of electric energy per ton of phosphorus produced (Stinson 1976). The furnace is water-cooled and has carbon-lined steel walls, a concrete or steel roof, and a carbon crucible. Its operating temperature is in the range of 1400°-1550° C (2252°-2822° F) (Barber 1980b).

The electrothermal reduction of phosphate rock produces a gaseous product consisting of approximately 90% carbon monoxide (CO), 7% phosphorus, and 3% other gases, primarily nitrogen, hydrogen, silicon tetrafluoride and dust. Furnace off-gas is routed on for cleaning and product recovery in another part of the plant. Ferrophosphorus, a by-product used by the metallurgical industry, and waste slag are also produced. These molten materials are intermittently tapped from one of two furnace tapholes in a molten state. Ferrophosphorus can be produced from the iron which naturally occurs in the phosphate rock, but iron slugs sometimes are added to the furnace burden to increase ferrophosphorus production. Slag consists mostly of calcium silicate and calcium aliminate and contains most of the impurities found in the original rock. Slag may be cooled with water or air but ferrophosphorus is strictly air-cooled since it is highly reactive with water and will burn or explode.

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Product Recovery

The gaseous mixture from the electric furnace is treated in an electrostatic precipitator to remove dust (Barber 1980b). Phosphorus vapor in the gas is condensed by adiabatic cooling with water sprays in an open chamber. Water and liquid phosphorus drain to a sump under the chamber where relatively pure liquid phosphorus settles to the bottom covered by a layer of water containing suspended particles of liquid phosphorus. The water and phosphorus mixture overflows into another compartment of the sump where additional liquid phosphorus settles out as the bottom layer. An emulsion, called phosphorus sludge, settles out as another layer, and the partially clarified (phossy) water is the top layer. Finally, the water flows to another compartment from which it is recycled to the condenser.

Uncondensed off-gases flow to a tubular condenser surrounded by cooling water. The mixture of condensed phosphorus and water drains to the phosphorus sludge compartment of the condenser sump. The gas is exhausted by a liquid-piston type of rotary blower. Recycled condenser water is used in the exhauster. Some phosphorus is collected by the exhauster, and the mixture of water and phosphorus drains to the spray water compartment of the sump.

Phosphorus condensing arrangements have not been standarized in the industry. Various combinations of spray and tubular condensers may be used. The objectives are to cool the gas as much as possible and to minimize formation of phosphorus sludge during the condensing process. When the gas is cooled to 50° to 55° C (122° to 131° F) by the condensing system, the operation is considered acceptable.

Phosphorus and phosphorus sludge are removed from the condenser sump by submerged pumps. Phosphorus and phosphorus sludge are kept separate. The phosphorus is a yellow liquid which will contain about 98 percent elemental phosphorus, but the quality will increase as impurities rise to the top as a sludge quality layer. Some producers filter phosphorus to obtain a higher quality product. The sludge collected in the condenser sump contains about one-third elemental phosphorus, one-third solid impurities, and one-third water. Both phosphorus and phosphorus sludges are stored under water to prevent burning, but in the case of phosphorus sludge the interface with water is not easily determined.

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The exhaust gas contains about 92.3% CO, 4.6% H_2, 2.1% N_2, 0.5% CO_2, and 0.3% CH_4 on a dry basis. The gas is saturated with both water and phosphorus at the condenser exhaust temperature. It has a heating value of about 300 Btu per cubic foot and may be burned in equipment such as dryers and kilns. The gas is needed as fuel in dryers and kilns, and combustion in boilers is not practiced. Without cleaning, combustion of the gas causes P_2O_5 to be emitted in the combustion gases.

Because liquid phosphorus autoignites on contact with warm air (93° C), it must be covered with water at all times to maintain a seal from the atmosphere. The phosphorus is kept under water both in the sump pit of the condenser tower and in the product storage tanks, but must be kept above its freezing point (44° C, 111° F) so that it can be removed. It must also be transported under a water blanket. Elemental phosphorus is only slightly soluble in water but the condenser water and water blanket pick up colloidal phosphorus which is very difficult to remove or treat. Disposal of this phosphorus-contaminated or "phossy" water is one of the industry's most serious environmental problems.

1.2.1.2 Phosphorus Consuming (Subcategory B)

Five major products are produced using elemental phosphorus from the electric furnace: phosphoric acid ("dry process" or furnace grade), phosphorus pentoxide, phosphorus pentasulfide, phosphorus trichloride, and phosphorus oxychloride. Various munitions are also produced from elemental phosphorus including white phosphorus and nerve gases known as GB and VX. However, the great majority (85%) of the industry's production of phosphorus is used to manufacture "dry process" phosphoric acid. Smaller quantities of other products are produced using anhydrous processes. Because phosphorus is transported and stored under a water blanket, phossy water may be a raw waste material at phosphorus-consuming plants as well as at phosphorus producing plants. The standard procedure for transferring liquid phosphorus from a rail car to the using plant's storage tank, however, is to pump the displaced phossy water from the storage tank back into the emptying rail car. Instead of being wasted at the phosphorus-using plant, the phossy water is shipped back to the phosphorus-producing facility for treatment and/or reuse.

Phosphoric Acid ("Dry Process")

In general, high quality "dry process" phosphoric acid is manufactured by burning phosphorus in air to produce phosphorus pentoxide and absorbing it in water to produce phosphoric acid (Figure 3). The following steps are involved in this process (USEPA 1977c):

- Molten phosphorus is sprayed into a combustion chamber with air or air and steam where it is burned. The combustion chamber is cooled by running water over the surface or by running phosphoric acid down the interior walls. The resulting gaseous mixture of phosphorus pentoxide and nitrogen may be cooled in a heat exchanger before being forwarded to the next process.

  An alternative to this process may be practiced in those cases where phosphorus is produced and consumed on the same site. The offgas from the electric arc furnace may be forwarded directly to the combustion chamber following cleaning where it is oxidized to phosphorus pentoxide (P_2O_5) and carbon dioxide (CO_2). This gas may then be cooled and forwarded on for the production of phosphoric acid.

- Mixed $P_2O_5/CO_2/N_2$ gases from off-gas combustion, or P_2O_5/N_2 gases from phosphorus combustion, are passed through an adsorption tower countercurrent to sprayed water. Acid mist is separated from the gas stream by means of a scrubbing tower, a cyclone, or a glass-wool filter.

- Phosphoric acid from the hydrator/absorption unit is purified by the addition of a soluble sulfide and silica and the filtration of the resulting precipitants. Arsenic and lead are precipitated by treatment with sulfide and silica is used to remove hydrofluoric acid. Arsenic and lead are removed by filtration.

- "Dry process" phosphoric acid may also be produced by contacting the combustion gases in the hydrator with dilute phosphoric acid rather than with water.

Phosphorus Pentoxide

Phosphorus pentoxide (P_2O_5) is produced by the rapid condensation of dry phosphorus combustion gases (Figure 4). The mixed P_2O_5/N_2 gases from the combustion of elemental phosphorus are forwarded to an externally cooled condensation chamber called a "barn." Solid phosphorus pentoxide condenses on the walls and is scraped from the walls by moving chains. It is removed from the hopper at the bottom of the "barn" by means of a screw conveyor.

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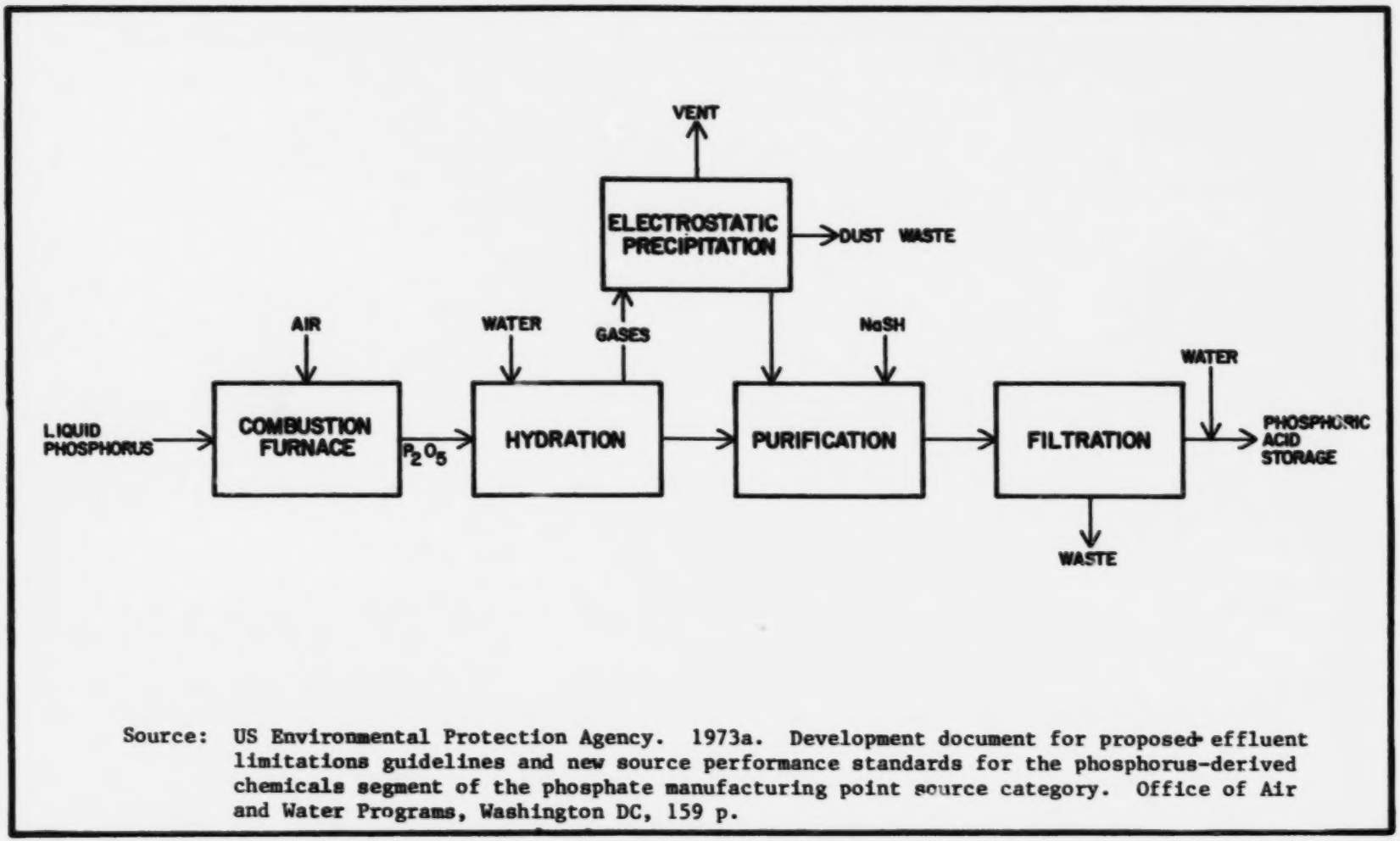
Figure 3. Standard process for production of "dry process" phosphoric acid.



Source: US Environmental Protection Agency. 1973a. Development document for proposed effluent limitations guidelines and new source performance standards for the phosphorus-derived chemicals segment of the phosphate manufacturing point source category. Office of Air and Water Programs, Washington DC, 159 p.

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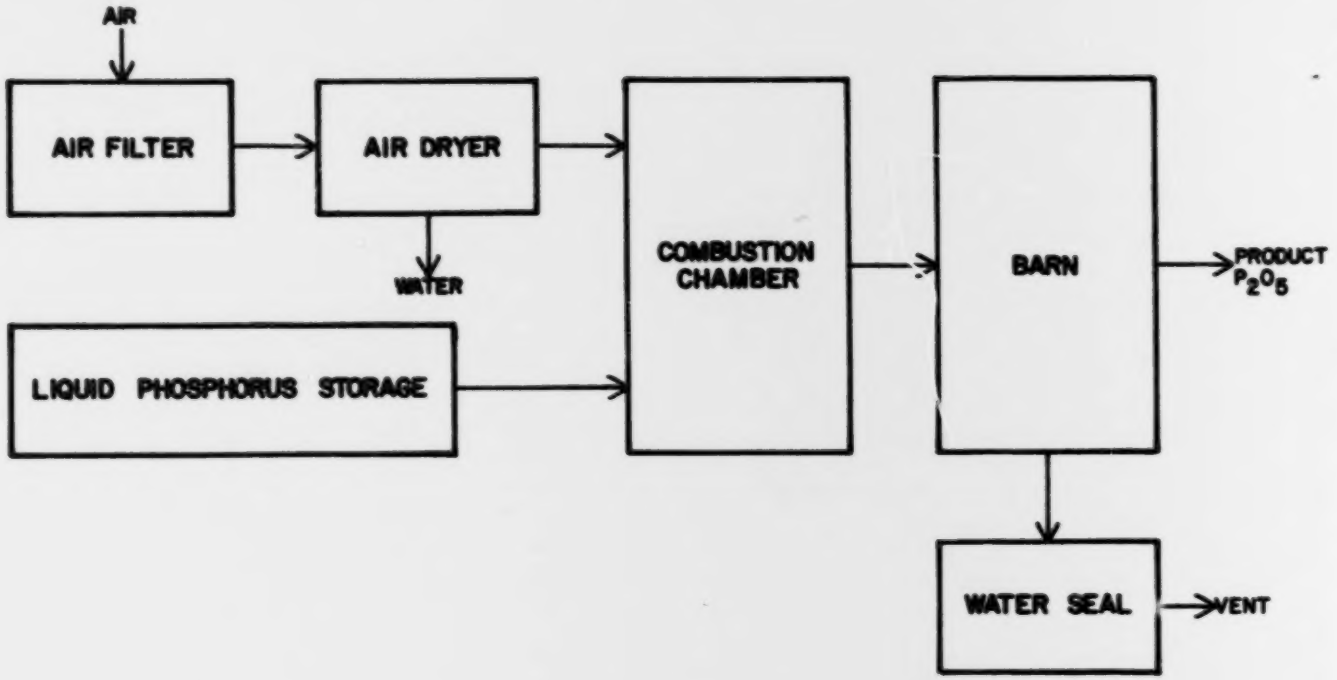
Figure 4. Standard process flow diagram for the manufacture of phosphorus pentoxide.



Source: US Environmental Protection Agency. 1973a. Development document for proposed effluent limitations guidelines and new source performance standards for the phosphorus-derived chemicals segment of the phosphate manufacturing point source category. Office of Air and Water Programs, Washington DC, 159 p.

Phosphorus Pentasulfide

Phosphorus pentasulfide (P_2S_5) is produced by mixing liquid phosphorus and liquid sulfur in a batch reactor (Figure 5). The reaction is highly exothermic and since both reactants are extremely flammable at the reaction temperature, the reactor must be constantly purged with nitrogen and the vent line must be water-sealed. The product is either casted and solidified directly from the holding tank or purified by vacuum distillation before casting. Since in its molten state P_2S_5 burns on contact with air, casting fumes are produced which must be removed. However, once the P_2S_5 is solidified, it no longer produces fumes and can be handled and stored.

Phosphorus Trichloride

Highly corrosive phosphorus trichloride (PCl_3) is produced in a water-cooled, jacketed batch reactor (Figure 6). Liquid phosphorus is charged into the reactor and gaseous chlorine is bubbled through it to produce phosphorus trichloride. The product is refluxed through the reactor until all of the phosphorus is consumed. The chlorine input must be carefully controlled to prevent production of phosphorus pentachloride. Following production of PCl_3, the product is batch distilled by the introduction of steam into the reactor jacket. The distillate is then condensed and collected. A semi-continuous variation of this process has also been developed.

Phosphorus Oxychloride

Phosphorus oxychloride ($POCl_3$) is manufactured by the reaction of phosphorus trichloride, chlorine, and solid phosphorus pentoxide in a jacketed batch reactor (Figure 7). Liquid phosphorus trichloride is charged into the reactor, solid phosphorus pentoxide is added, and chlorine is bubbled through the mixture. Following reaction, steam is supplied to the reactor jacket, water to the reflux condenser is shut off, and the product is distilled from the reactor and collected. An alternate process also is in commercial use which involves air oxidation of phosphorus trichloride to produce the oxychloride form.

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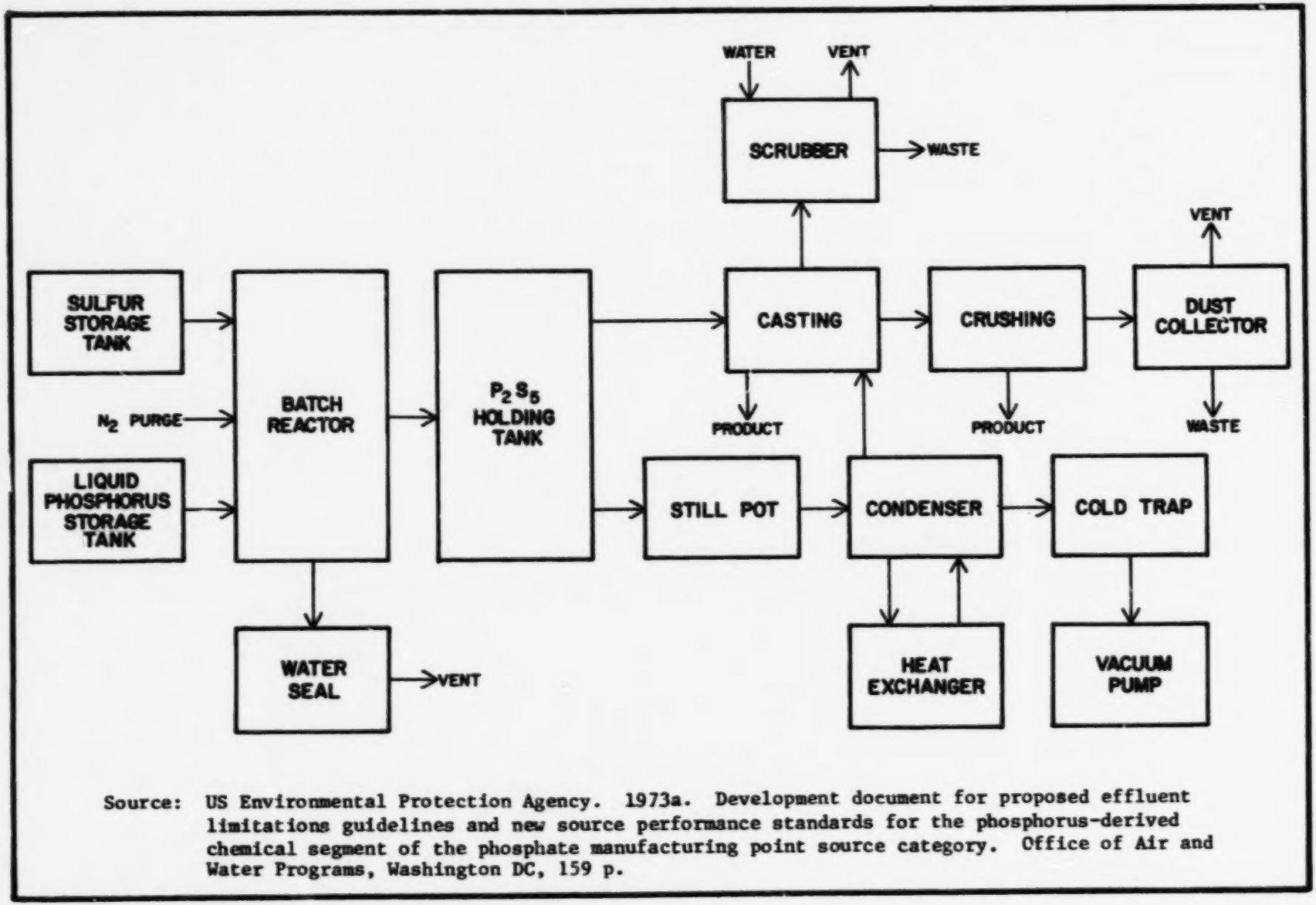
Figure 5. Standard process flow diagram for the manufacture of phosphorus pentasulfides.



Source: US Environmental Protection Agency. 1973a. Development document for proposed effluent limitations guidelines and new source performance standards for the phosphorus-derived chemical segment of the phosphate manufacturing point source category. Office of Air and Water Programs, Washington DC, 159 p.

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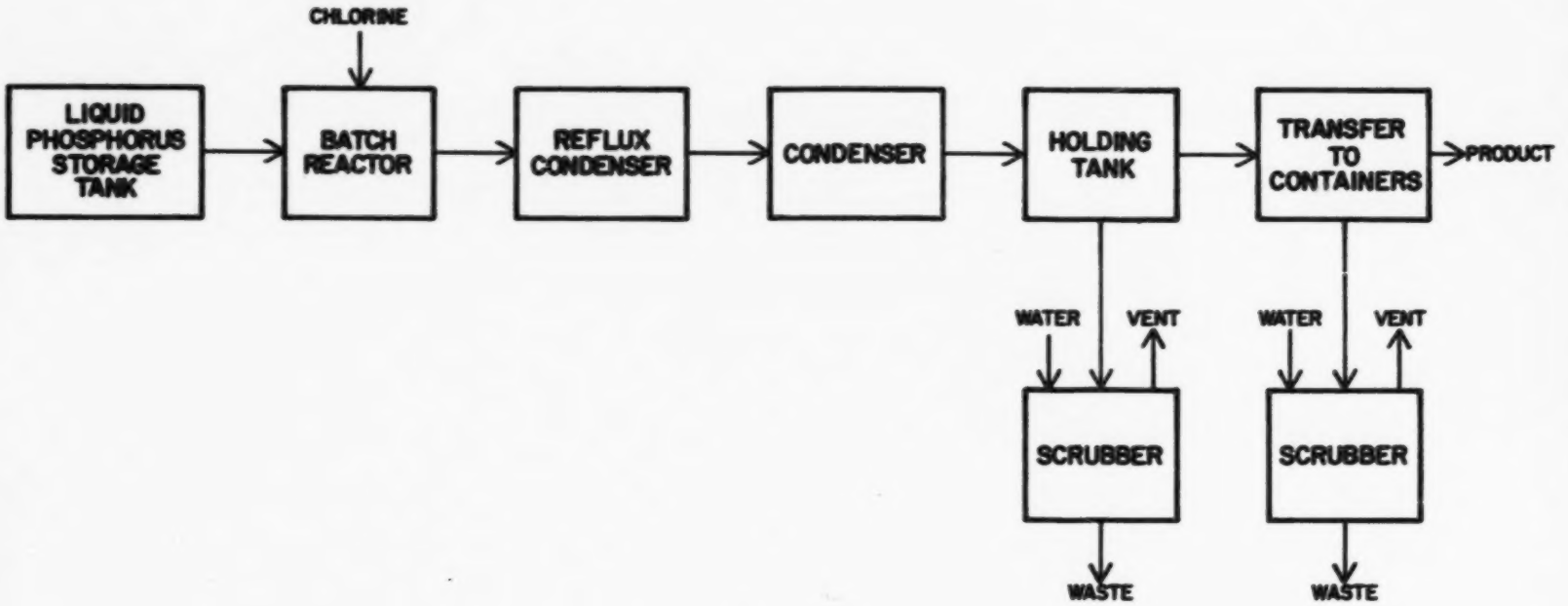
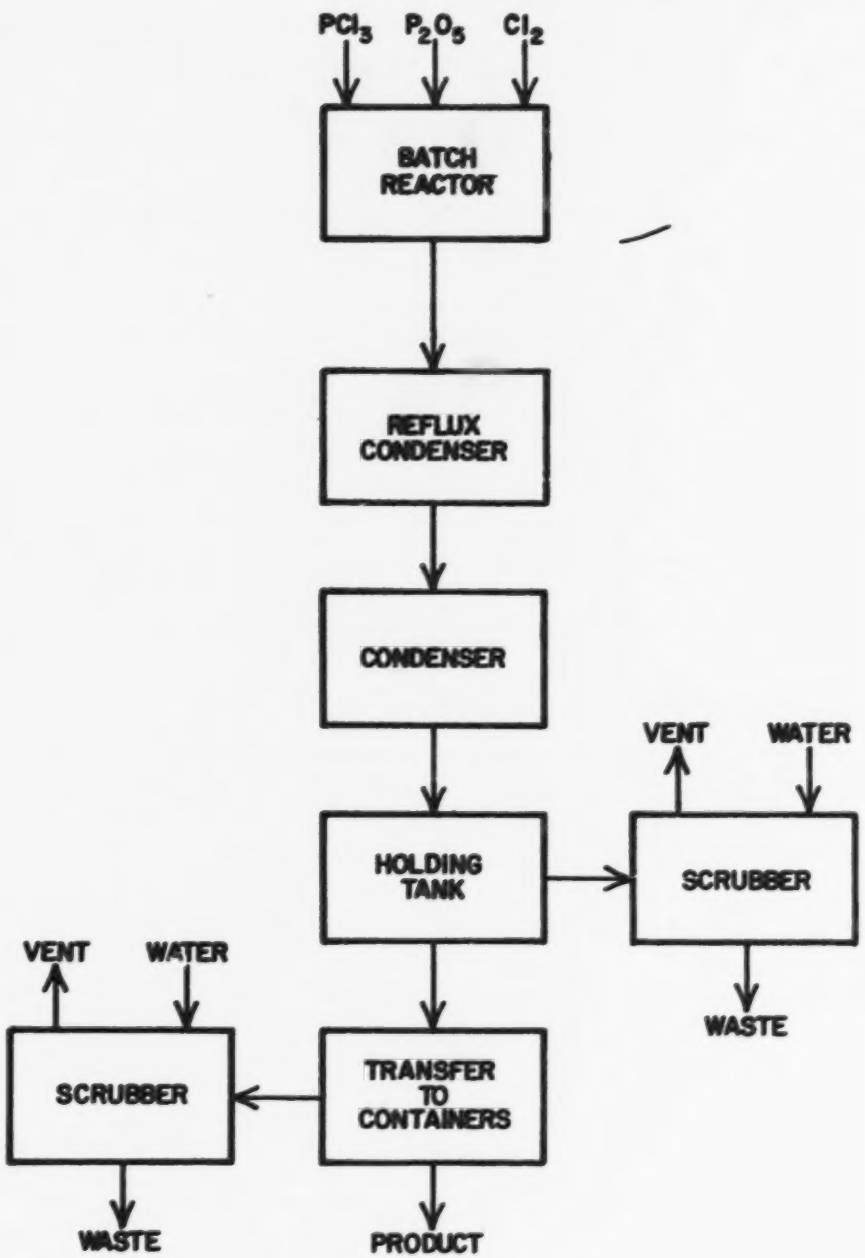
Figure 6. Standard process flow diagram for the manufacture of phosphorus trichloride.



Source: US Environmental Protection Agency. 1973a. Development document for proposed effluent limitations guidelines and new source performance standards for the phosphorus-derived chemicals segment of the phosphate manufacturing point source category. Office of Air and Water Programs, Washington DC, 159 p.

Figure 7. Standard process flow diagram for the manufacture of phosphorus oxychloride.



Source: US Environmental Protection Agency. 1973a. Development document for proposed effluent limitations guidelines and new source performance standards for the phosphorus-derived chemicals segment of the phosphate manufacturing point source category. Office of Air and Water Programs, Washington DC, 159 p.

1.2.1.3 Phosphate Chemicals (Subcategory C)

The products of this subcategory are primarily high quality sodium tripolyphosphate and high grade calcium phosphate for use in food or personal products. The sodium phosphates produced from "dry process" acid are used primarily in the manufacture of detergents due to their low coloration and purity. Feed grade and human food grade calcium phosphate are usually manufactured from "dry process" acid due to the obvious purity requirements of these products.

Sodium Phosphates

A number of sodium phosphate compounds including tetrasodium pyrophosphate ($Na_4P_2O_7$), sodium acid pyrophosphate ($Na_2H_2P_2O_7$), and disodium orthophosphate are made in small quantities, but the largest volume sodium phosphate products are sodium tripolyphosphate and sodium orthophoshpate. Sodium tripolyphosphate is considered by some to be the ideal builder for use in detergents and is the major product of this segment of the industry. It is a water softener, emulsifier, soil dispersant, buffering agent and is non-irritating (USDOC 1980). The process for the manufacture of sodium tripolyphosphate as shown in Figure 8 involves the neutralization of "dry process" phosphoric acid with either soda ash (Na_2CO_3) or a mixture of soda ash and caustic soda (NaOH) followed by crystallization and calcination of the mono- and disodium products to a condensed form. Sodium orthophosphate products are made by slight variations of the same processes. These steps are described in more detail below (USEPA 1977c):

- The manufacture of all sodium phosphate products begins as a common process. Phosphoric acid is first neutralized in a batch reactor with a slight excess of soda ash (Na_2CO_3) or a caustic and soda ash mixture. This solution is then boiled with steam until all of the carbon dioxide is driven off. The disodium orthophosphate (Na_2HPO_4) solution is then filtered to remove silica, iron, and aluminum phosphates. The final solution is then prepared by addition of phosphoric acid or acid and caustic soda (NaOH) corresponding to the pH and composition of the desired product.
- To produce monosodium orthophosphate the sodium phosphate solution is diluted with H_3PO_4 to give a solution corresponding to NAH_2PO_4 and evaporated to form the desired product in a dessicated, crystalline form.

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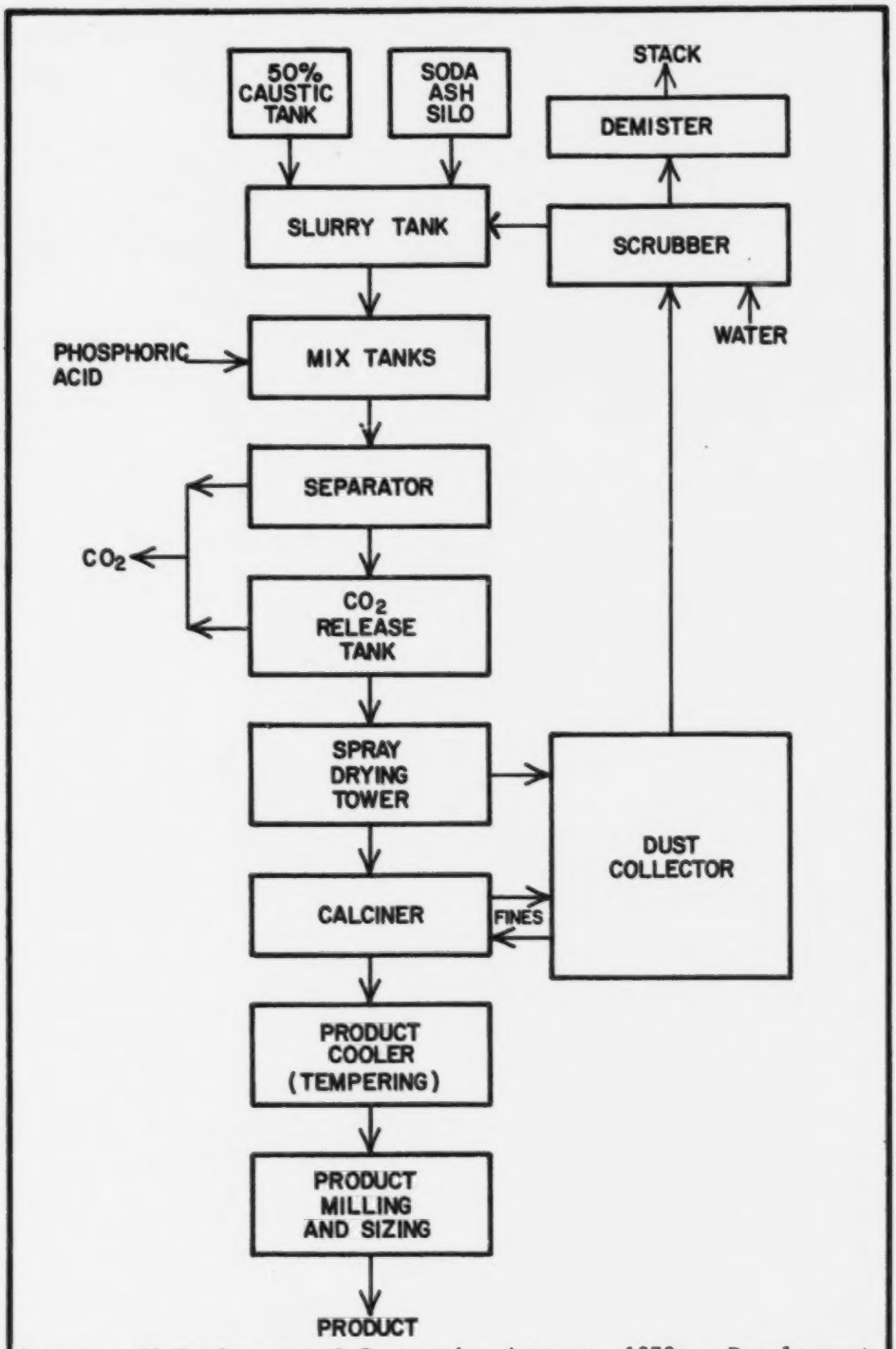
Figure 8. Standard process flow diagram for the manufacture of sodium tripolyphosphate from "dry process" phosphoric acid.



Source: US Environmental Protection Agency. 1973a. Development document for proposed effluent limitations guidelines and new source performance standards for the phosphorus-derived chemicals segment of the phosphate manufacturing point source category. Office of Air and Water Programs, Washington DC, 159 p.

- To produce disodium orthophosphate (Na_2HPO_4) the solution is crystalized and the crystals are separated by centrifugation. Process solutions are returned to the neutralization stage and the crystals are dried to $Na_2HPO_4 2H_2O$ or Na_2HPO_4.

- Sodium tripolyphosphate ($Na_5P_3O_{10}$) is produced by the calcination of a solution or mixture of mono- and disodium orthophosphate in a rotary kiln. Following calcination, vitreous sodium tripolyphosphate is annealed to prevent the phosphates from reverting to a different form.

- Vitreous sodium orthophosphate products are produced by feeding mono- and disodium phosphate solutions into a furnace. A molten solid forms which must be chilled and ground into the final product.

Calcium Phosphates

In general, non-fertilizer calcium phosphates are made by the neutralization of phosphoric acid with lime. The processes for two of the major products are indicated in Figures 9 and 10 which show the processes for various human food grade calcium phosphates and animal feed grade calcium phosphates respectively. Although the processes for production of all calcium phosphate compounds are chemically similar, they differ in the amount and grade of lime and phosphoric acid used and in the volume of process water required. "Dry process" or furnace grade phosphoric acid must be used in the production of human food grade calcium phosphates, while defluorinated "wet process" phosphoric acid is acceptable for animal feeds (USEPA 1977c).

Generalized descriptions of the processes for production of the various calcium phosphate products are provided below (USEPA 1977c):

- Monocalcium phosphate monohydrate (MCP) ($CaH_4(PO_4)_2H_2O$) is formed by mixing an excess of 75% dry process phosphoric acid with a lime slurry. An excess of acid is maintained to prevent formation of dicalcium phosphate. A small amount of steam is liberated from the process due to heat of reaction.

- Anhydrous monocalcium phosphate (MPC) ($CaH_4(PO_4)_2$) is produced by the reaction of quicklime with dry process phosphoric acid at 140° C in a batch mixer. At higher heat the water is driven off as it is produced. A small amount of aluminum phosphate or potassium and sodium phosphates are included in the mix. After heat treatment, these additives form protective coatings on the surface of the $CaH_4(PO_4)_2$ crystals.

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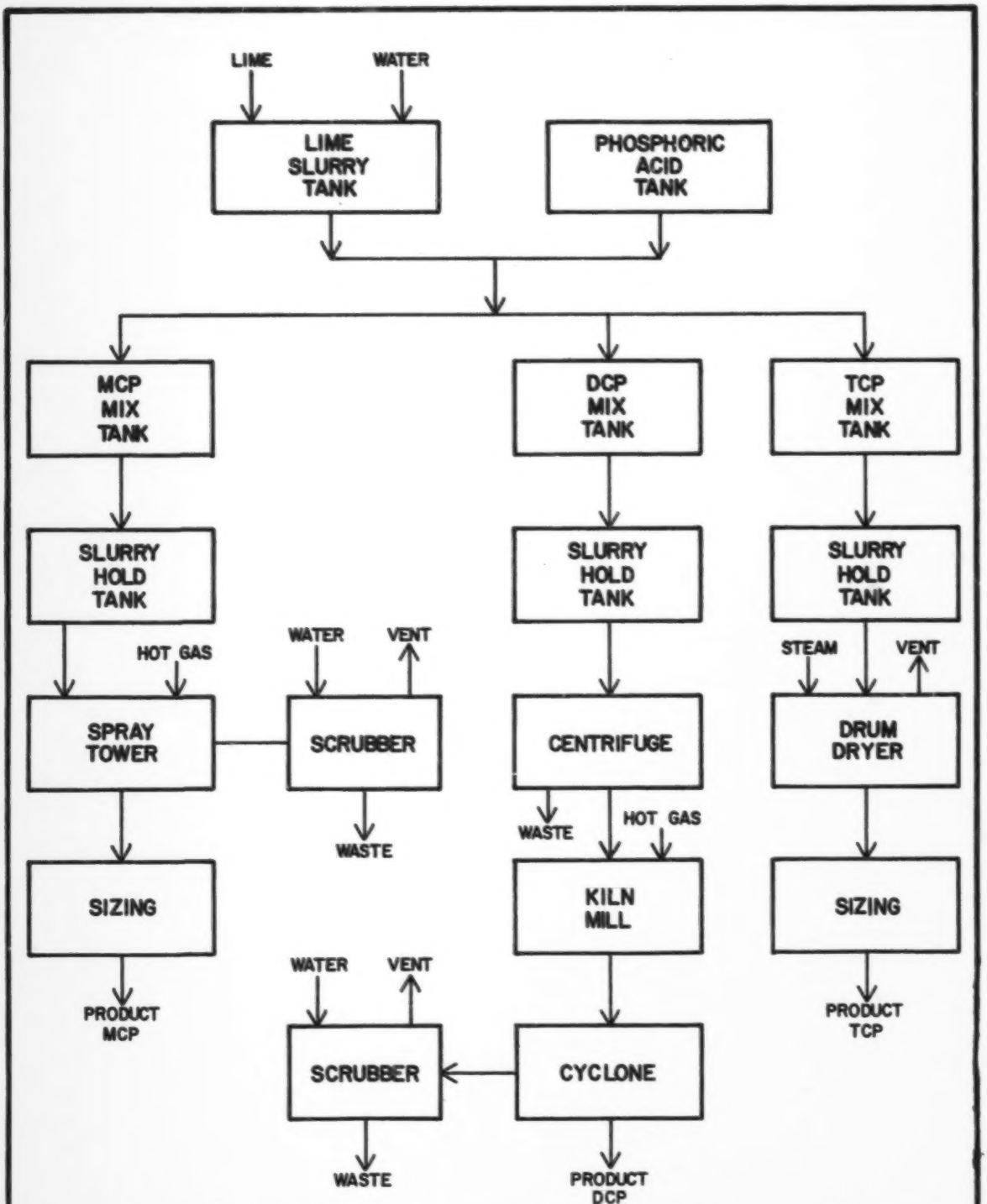
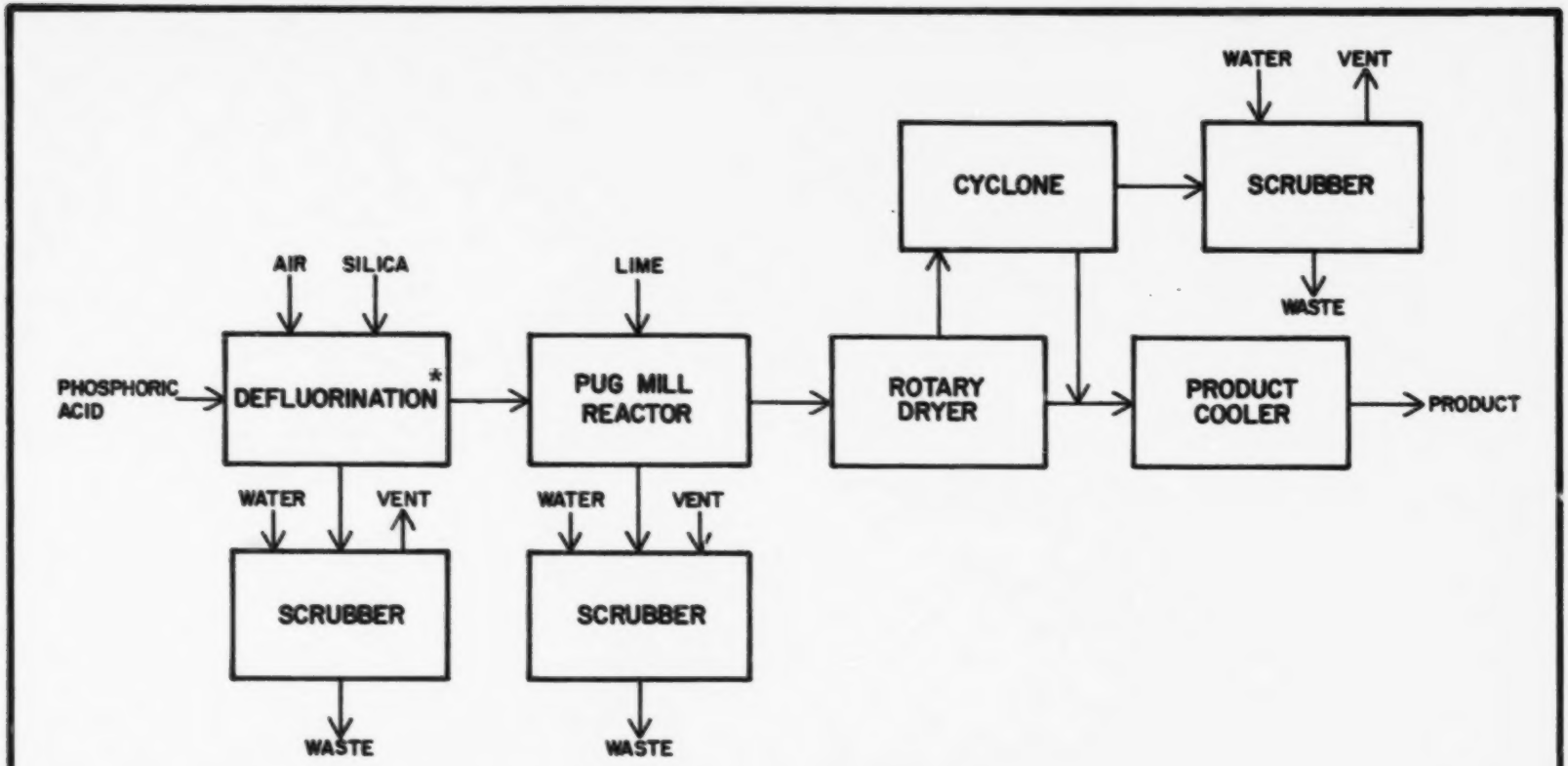
Figure 9. Standard process flow diagram for the manufacture of food grade calcium phosphates from "dry process" phosphoric acid.



Source: US Environmental Protection Agency. 1973a. Development document for proposed effluent limitations guidelines and new source performance standards for the phosphorus derived chemicals segment of the phosphate manufacturing point source category. Office of Air and Water Programs, Washington DC, 159 p.

Figure 10. Standard process flow diagram for the manufacture of animal feed grade calcium phosphates from "wet process" phosphoric acid.



Source: US Environmental Protection Agency. 1973a. Development document for proposed effluent limitations guidelines and new source performance standards for the phosphorus-derived chemicals segment of the phosphate manufacturing point source category. Office of Air and Water Programs, Washington DC, 159 p.

* Defluorination of phosphoric acid is a separate process described in Subcategory E.

- Dicalcium phosphate dihydrate (DCP) ($CaHPO_4 2H_2O$) is produced by mixing a dilute lime slurry with dilute dry process phosphoric acid and dissipating the heat of the reaction. An excess of water is used in this process to assure a homogenous mixture and a correct stoichiometric balance among the reactants. The product must be centrifuged to remove excess water prior to drying.

- Dicalcium phosphate for animal feed is manufactured with purified wet process phosphoric acid and powdered limestone in a pug mill reactor without excess water since a higher concentration of mono- and tricalcium phosphates are acceptable in animal feed.

- Tricalcium phosphate (TCP) ($Ca_3(PO_4)_2$) is prepared by adding phosphoric acid to a slurry containing an excess of lime to prevent formation of DCP.

- Finishing operations Following the initial reaction, calcium phosphate products are dried or further processed as follows (USEPA 1977c). Monocalcium phosphate monohydrate ($CaH_4(PO_4)_2H_2O$) thick slurry is usually dried in a spray tower or vacuum dryer. Anhydrous monocalcium phosphate ($CaH_4(PO_4)_2$) is heat-treated to change the protective coatings (formed by aluminum phosphate or potassium plus sodium phosphate) from orthophosphates to polyphosphates. Dicalcium phosphate dihydrate ($CaHOP_4 2H_2O$) must be dried in a tube dryer or kiln mill if powdered limestone is the source of calcium in the compound. If quicklime is used as the calcium source, no drying is necessary. Tricalcium phosphate slurry is filtered and dried.

1.2.1.4 Defluorinated Phosphate Rock (Subcategory D)

Apatite phosphate rock contains sufficient calcium and phosphorus to be a useful animal feed supplement but the 3-4% fluorine that it contains must be removed first to avoid its toxic effects. Three methods have been developed for defluorinating phosphate rock commercially: 1) acidulation and heat treatment of phosphate rock, 2) furnace volatilization of fluoride, and 3) calcination of phosphate rock. Of these, calcination is the most commercially favorable and is the process most commonly used. Details regarding these processes are trade secrets and not generally available but they may be described generally as follows (USEPA 1976a):

Acidulation

Defluorinated phosphate rock may be produced by reacting phosphate rock with sulfuric acid and heating the resultant superphosphate to volatilize the

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fluorine. This process is similar to the production of normal superphosphate in the fertilizer industry. The phosphate product is in the form of tricalcium phosphate.

Furnace Volatilization

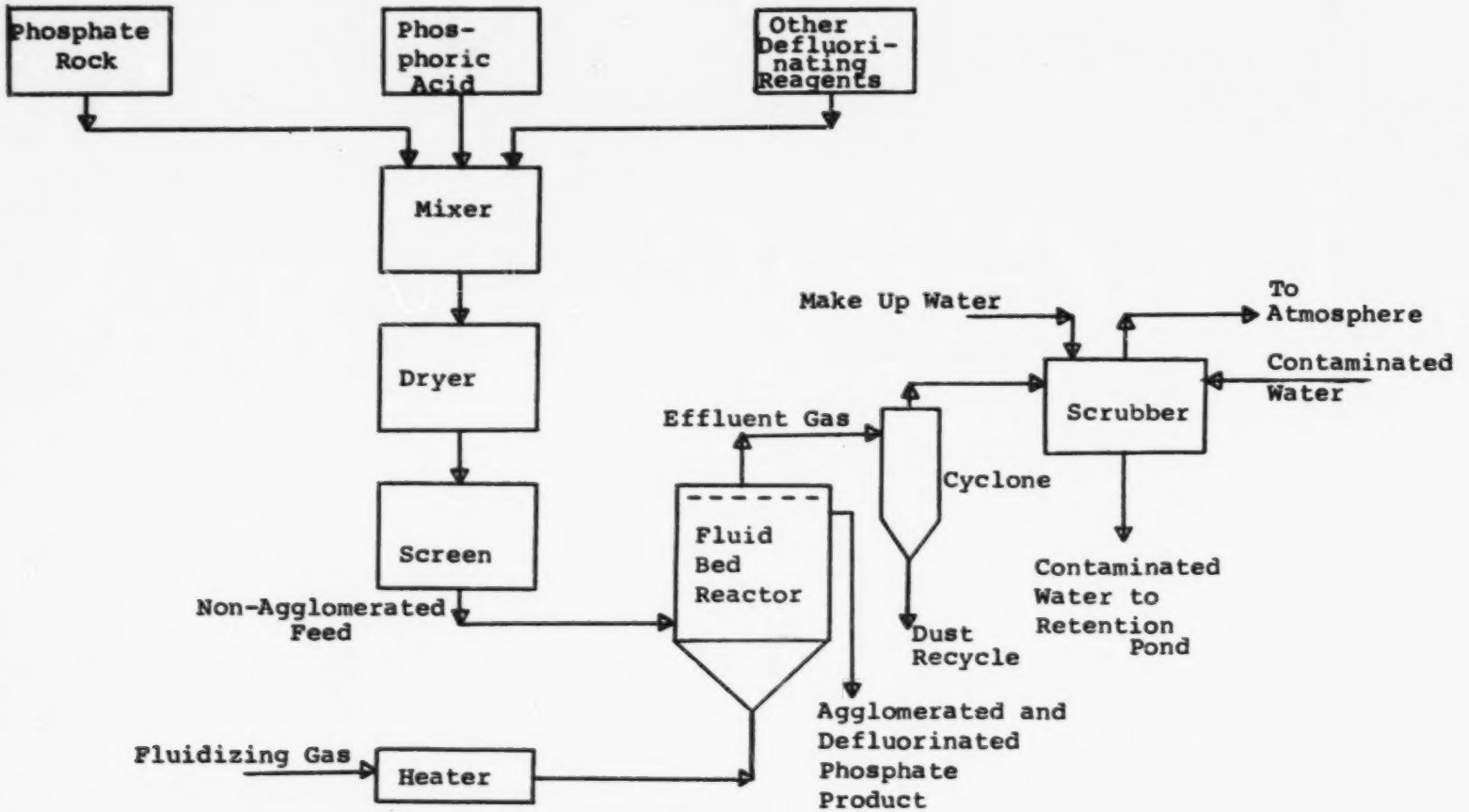
Fluorine may also be removed from phosphate rock by heating a rock and silica mixture in an oil-fired shaft furnace to agglomerate the mixture and drive off the fluorine. The hot mass is quenched with water as it is removed from the furnace.

Calcination

The predominant commercial phosphate rock defluorination process in the United States involves calcination of a phosphate rock/silica/soda ash/and phosphoric acid mixture in a rotary kiln or fluid bed reactor (Figure 11). The charge for the fluid bed reactor, the more widely used of the two reactors, is a combination of phosphate rock silica, soda ash, and other defluorinating agents which is treated with phosphoric acid and dried to form a nodular charge. The nodular, predried charge is used to effect particle classification in the bed and aid the loss of exhaust gases. Exhaust gases are cleaned to remove dust and fluoride compounds evolved during calcination. The rotary kiln may receive its charge either as a physical mixture or in a nodular form. From the kiln or reactor, the defluorinated product is quickly quenched with air or water, then crushed and sized. The rapid quenching following calcination maintains the tricalcium phosphate product in the more highly soluble alpha form.

Critical operating criteria for this process include temperature, retention time, and water vapor content. Reaction temperatures are maintained in the range of 1,205-1,360° C for 30 to 90 minutes with the fluid bed reactor operating at the lower temperatures and requiring less time. Water vapor content must also be maintained at a level sufficient to effect evolution of fluorine. Dehydrated tricalcium phosphate is formed in the kiln. Gaseous silicon fluoride is liberated during calcination and is hydrolyzed to silica and hydrofluoric acid by the tail gas exhaust scrubber.

Figure 11. Process flow diagram for the manufacture of defluorinated phosphate rock by the fluid bed calcination process.



Source: US Environmental Protection Agency. 1976a. Development document for effluent limitations guidelines and new source performance standards for the other non-fertilizer phosphate chemicals segment of the phosphate manufacturing point source category. Office of Water and Hazardous Materials, Washington DC, 105 p.

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1.2.1.5 Defluorinated Phosphoric Acid (Subcategory E)

Defluorinated phosphoric acid is used in the manufacturing of both dry and liquid mixed fertilizers and in the production of dicalcium phosphate animal feed supplements. However, the majority of the defluorinated phosphoric acid produced in this country is used in the manufacture of fertilizer (USEPA 1976a).

There are three commercial methods for production of defluorinated acid. The most common method is vacuum evaporation. Aeration and submerged combustion also have been successfully used but submerged combustion is considered outmoded and is not likely to be used in the future for new facilities.

Vacuum Evaporation

The defluorination of phosphoric acid by vacuum evaporation is an example of crossover technology from the fertilizer industry. In fact, the same units are used by the fertilizer industry for evaporating commercial wet process 54% P_2O_5 phosphoric acid to superphosphoric acid (68-72% P_2O_5) as are used for defluorination of phosphoric acid. Approximately 86% of the defluorinated phosphoric acid in the United States is produced by the fertilizer industry (USEPA 1974b), but to the fertilizer industry defluorination is merely an accessory (or additional) side benefit accomplished during superphosphoric acid production. However, phosphoric acid is defluorinated specifically for the production of non-fertilizer products in a few places.

In the vacuum evaporation process, water and other contaminants including fluorine are evaporated from the acid using heat transfer surfaces and low (vacuum) pressure. Two of the most popular variations of this process are the Stauffer falling film evaporator and the Swenson forced circulation evaporator. These two processes are described below and shown schematically in Figures 12 and 13 respectively.

In the Stauffer process, clarified 54% P_2O_5 orthophosphoric acid is continuously fed to the evaporator recycle tank where it mixes with superphosphoric acid from the evaporator. Some of the mixture (approximately 1.2%) is

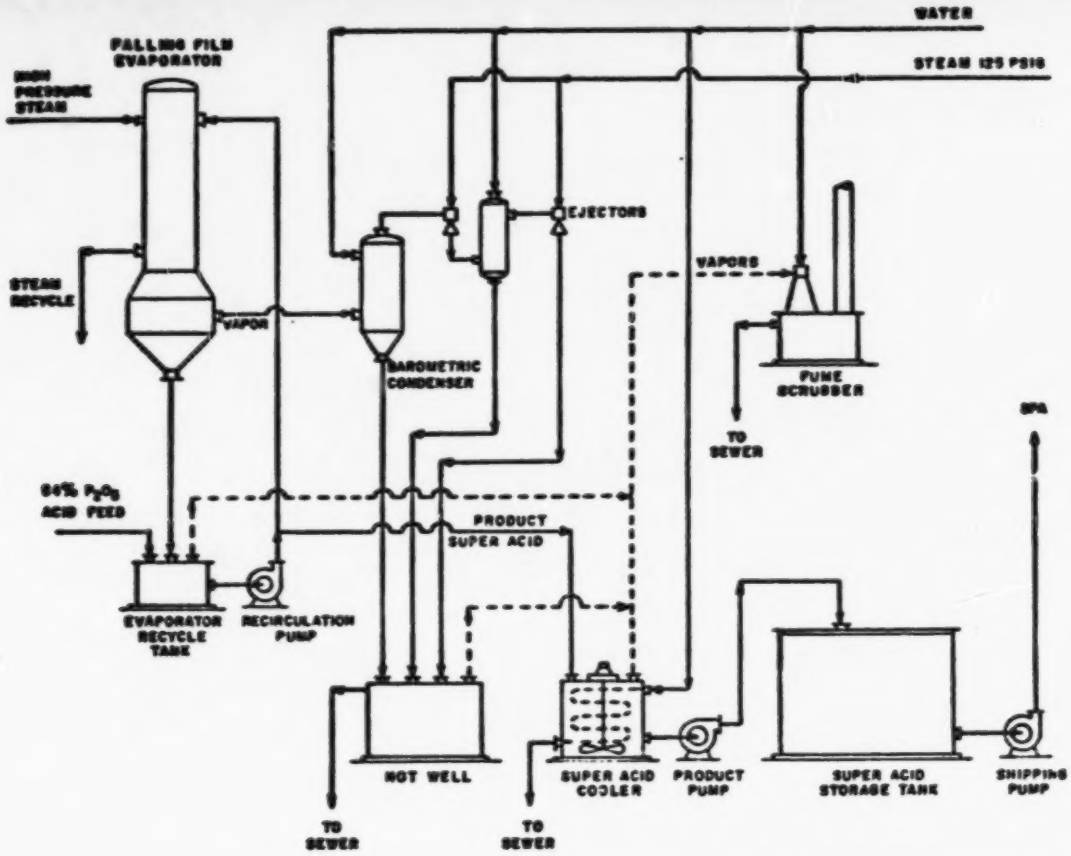

Figure 12. Stauffer process for wet process superphosphoric (deflourinated) acid.

Source: Barber, J.C. 1979. Falling film evaporator process. Adapted from TVA file drawings. Florence AL.

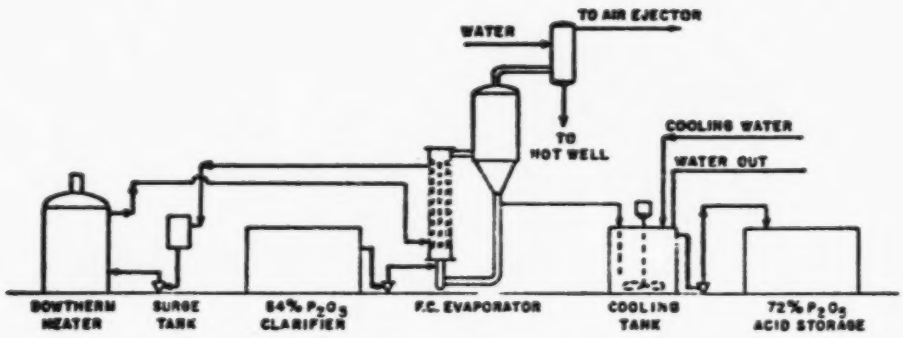

Figure 13. Vacuum evaporation superphosphoric (deflourinated) acid.

Source: Adapted from Rushton, W.E. 1966. Swenson superphosphoric acid process. Phosphorus and Potassium 23:13-16, 19.

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drawn off as product acid, but most (approximately 98.8%) is pumped to the top of the evaporator and is distributed across the heat exchanger tube bundle. The falling acid, heated by high-pressure steam condensing on the outside of the tubes, evaporates. The vapors and dehydrated acid then enter the separator section where entrained acid mist is removed. Product acid flows to the recycle tank, and the vapor is drawn off, condensed in a barometric condenser, and delivered to a hot well. Noncondensables are removed by a two-stage steam ejector and are vented to the hot well. Superphosphoric acid flows to the recycle tank where it is mixed with more 54% P_2O_5 orthophosphoric acid and recycled or removed as product. The approximate recycle to feed acid ratio is 80:1. The product stream is cooled and stored before shipping. Both the hot well and cooling tank are vented to a wet scrubbing system.

The Swenson process utilizes closed heat exchanger tubes filled with heat exchanger fluid to provide the heat of reaction. Feed acid (54% P_2O_5) pumped into the evaporating system mixes with recycled superphosphoric acid. As the acid leaves the exchanger tube bundle and enters the flash chamber, evaporation begins. Vapors are removed by a barometric condenser. Condensed materials and noncondensed vapors are delivered to a hot well. Product acid flows toward the bottom of the flash chamber where part (approximately 0.6%) is removed to a cooling tank and the rest (99.4%) is recycled. An approximate recycle to feed ratio is 150:1 (compared with 80:1 for the Stauffer process).

Cooling in both systems is accomplished by circulating water through stainless steel tubes in the holding tank.

Impurities in "wet process" acid, such as iron and aluminum phosphates, soluble gypsum, and fluosilicates, form supersaturated solutions in 54% P_2O_5 phosphoric acid and precipitate during storage. The precipitated impurities are separated from the acid by settling and/or centrifugation and either sent to the recirculation pond, processed into a low quality fertilizer, or recycled to the evaporator feed tank (USEPA 1979b).

Submerged Combustion

Although this process is outmoded and an unlikely option for any new facility, it is presented to give the reader an alternative perspective on the process. The submerged combustion apparatus consists of a combustion chamber with one or more gas or fuel oil burners mounted atop an acid vat called the evaporator (See Figure 14). Heat is transferred by inserting the dip tubes into the evaporator which bubble hot combustion gases through the acid and strip hydrogen fluoride and silicon tetrafluoride from the solution. Acid concentration is also achieved through evaporation of water. The production of a continuous product stream is controlled by feed acid flow and the acid temperature in the evaporator.

Gaseous emissions from this process are significant and require a series of cleaning and adsorption steps to effect product recovery and control air pollution. Entrained phosphoric acid first is recovered from the gas stream and recirculated or returned to the product line. A multistage direct contact condenser or a scrubber and gas filter is then used for removal of fluorides before the tail gas is exhausted. Water may be used in all or only the final stage of the condenser as a condensing and scrubbing medium.

Aeration

A relatively new method of defluorinated phosphoric acid production has been introduced in which fluorine is stripped from the acid by aeration (Figure 15). Small quantities of either diatomaceous silica or spray-dried silica gel are mixed with commercial 54% P_2O_5 phosphoric acid and heated. Silica reacts with the small amount of hydrogen fluoride in the acid to produce fluosilicic acid (H_2SiF_6). When the mixture is heated, the fluosilicic acid breaks down to tetrafluorosilane (SiF_4) which is stripped from the acid by aeration. The gas evolved during aeration is kept above its dew point and sent to a water scrubbing unit where the tetrafluorosilane is removed from the tail gas before discharge.

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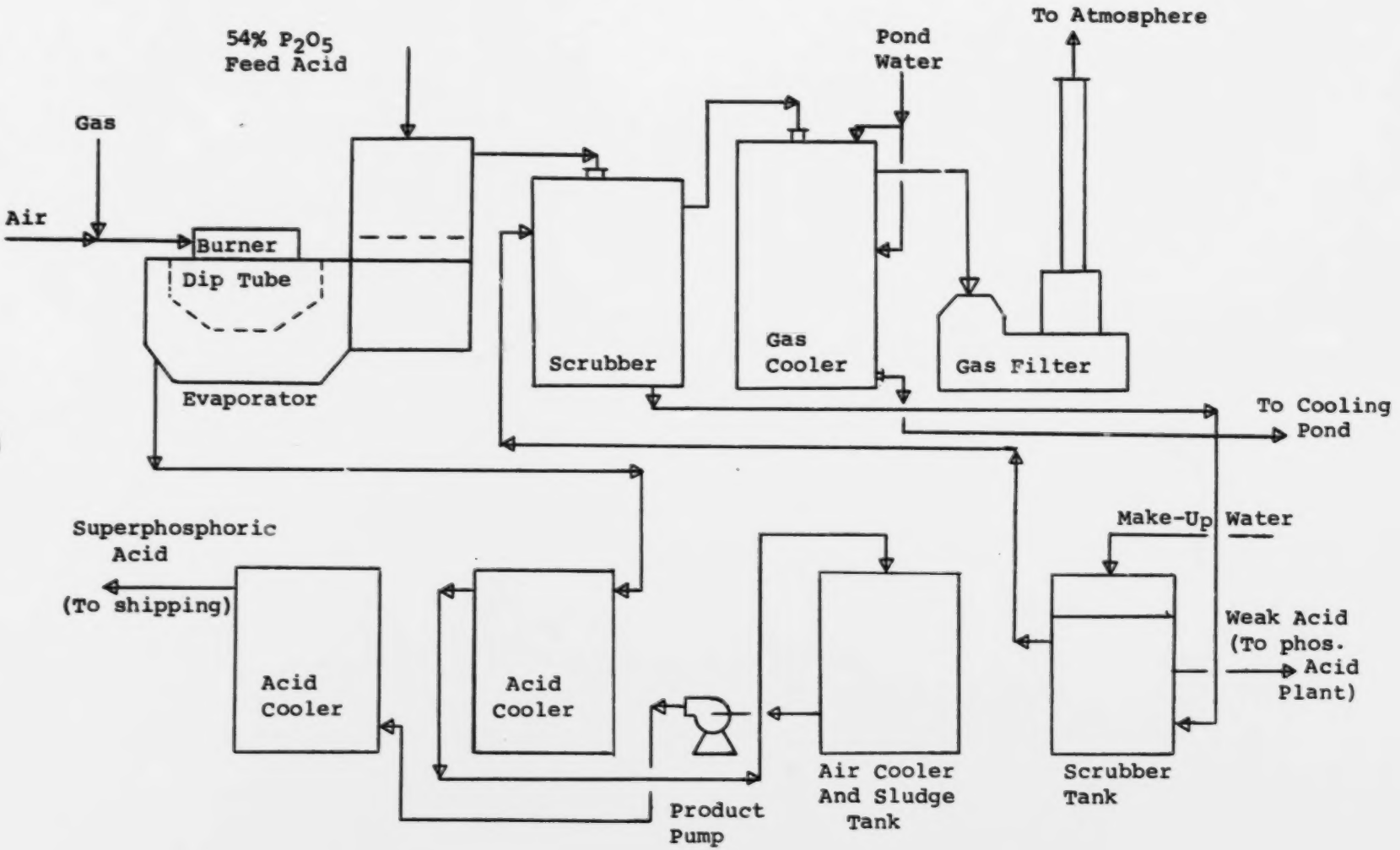
Figure 14. Process flow diagram for the manufacture of defluorinated phosphoric acid by the submerged combustion process.



Source: US Environmental Protection Agency. 1976a. Development document for effluent limitations guidelines and new source performance standards for the other non-fertilizer phosphate chemicals segment of the phosphate manufacturing point source category. Office of Water and Hazardous Materials, Washington DC, 105 p.

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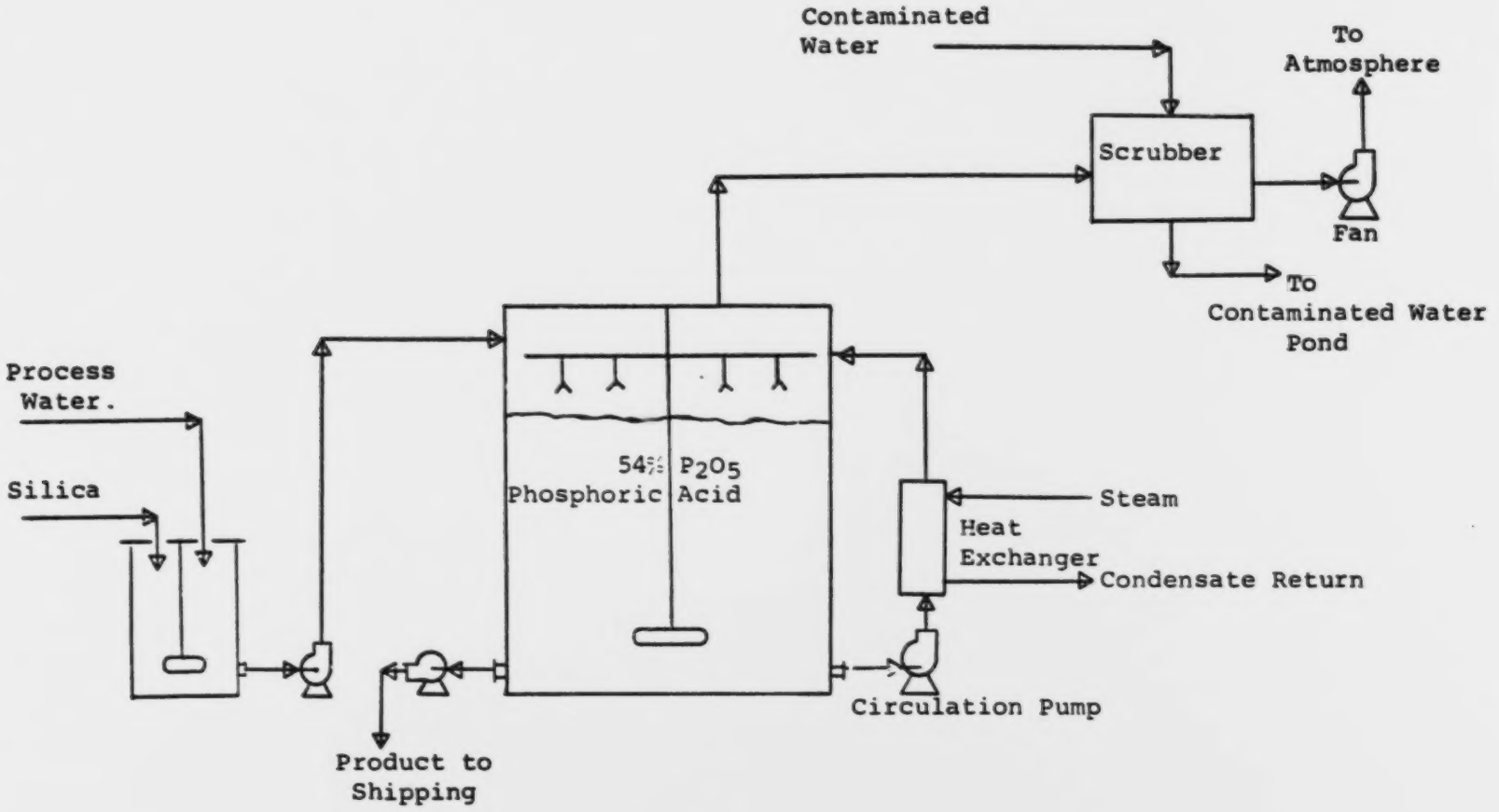
Figure 15. Process flow diagram for the manufacture of defluorinated phosphoric acid by the aeration process.



Source: US Environmental Protection Agency. 1976a. Development document for effluent limitations guidelines and new source performance standards for the other non-fertilizer phosphate chemicals segment of the phosphate manufacturing point source category. Office of Water and Hazardous Materials, Washington DC, 105 p.

1.2.1.6 Sodium Phosphate from "Wet Process" Phosphoric Acid (Subcategory F)

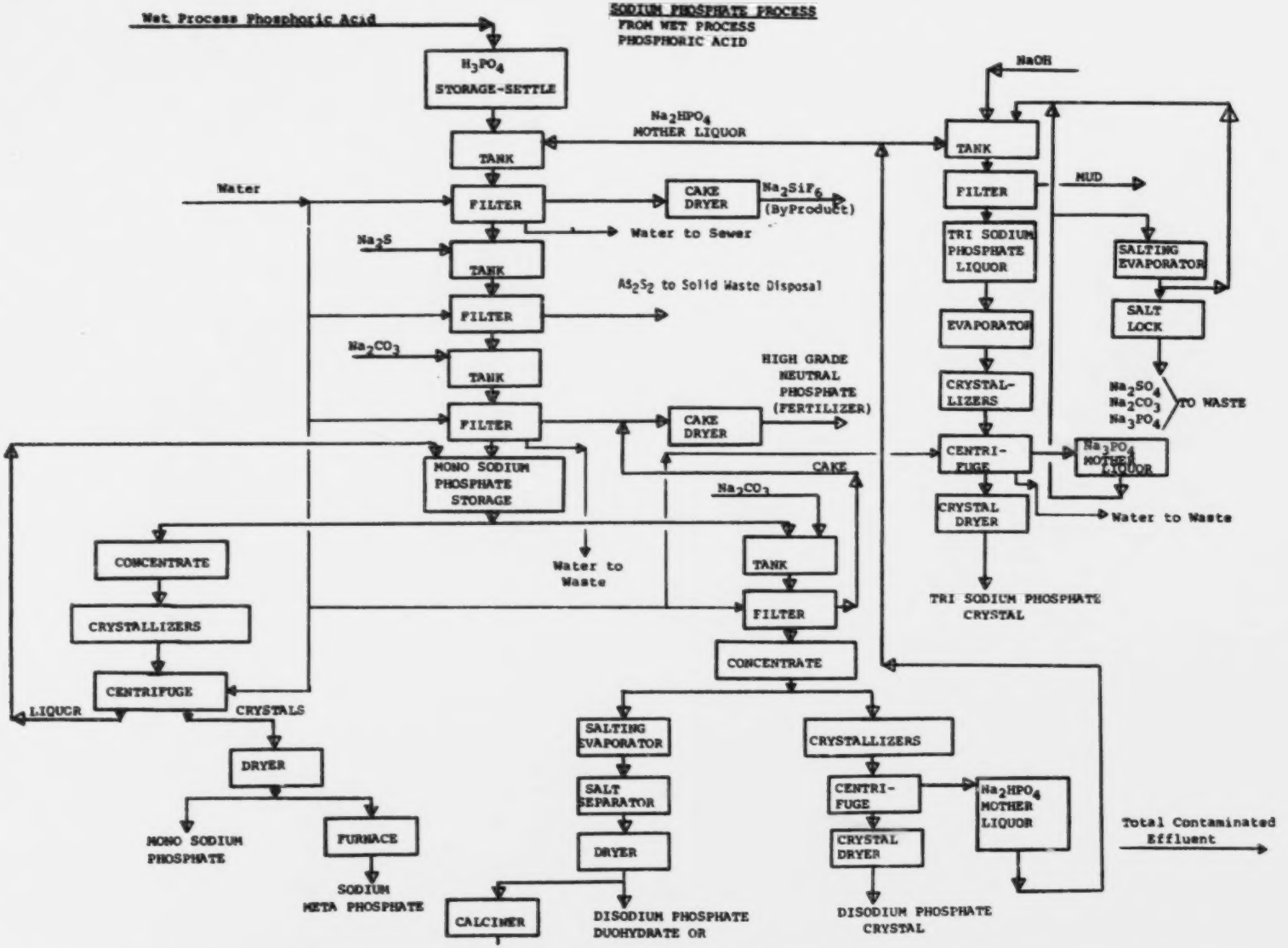
Most high grade sodium phosphate is made from dry process phosphoric acid because of the purity and product color requirements of the industry. Although limited in production to one plant at present, "wet process" acid can be purified sufficiently to manufacture sodium phosphate for soap (Figure 16). This process removes the more significant contaminants such as sulfuric acid, sodium fluosilicate, iron phosphate, aluminum phosphate, and calcium sulfate--as well as some of the minor impurities such as arsenic--and yields an acceptable quality product.

In order to manufacture high quality sodium phosphates by this process, the phosphoric acid must be prepared from phosphate rock which has been calcined to remove organic impurities that would give the acid a greenish color typical of "wet process" phosphoric acid. The nearly colorless "wet process" acid is partially neutralized with partially recycled sodium phosphate liquor to precipitate granular sodium fluosilicate which is sold as a by-product. After filtration of the sodium fluosilicate, sodium sulfide and barium carbonate are added. The sodium sulfide precipitates the small amount of arsenic found in wet process acid and the barium carbonate is added to remove excess sulfate. The precipitates are filtered and disposed of. Because of its toxic nature, arsenic sludge must be disposed of in an approved hazardous waste disposal site or reprocessed to recover the arsenic. A final neutralization of the acid is performed by the addition of soda ash (Na_2CO_3) to remove the remaining impurities. This procedure produces a large volume of light sludge containing iron phosphate, aluminum phosphate, and fluorine compounds. Although difficult to separate, the solid impurities from this final neutralization contain a relatively high concentration of phosphate and have some commercial value. Monosodium phosphate is crystalized from the acid by concentrating the solution in an evaporator. Other sodium phosphate compounds may be made from the monosodium phosphate with further dehydration, crystallization, and neutralization as described under subcategory C.

1.2.2 Auxiliary Processes

The non-fertilizer phosphate industry is closely linked to the phosphate mining and fertilizer industries. A brief background description of certain

Figure 16. Process flow diagram for the manufacture of sodium phosphates from "wet process" phosphoric acid.



Source: US Environmental Protection Agency. 1976a. Development document for effluent limitations guidelines and new source performance standards for the other non-fertilizer phosphate chemicals segment of the phosphate manufacturing point source category. Office of Water and Hazardous Materials, Washington DC, 105 p.

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related operations from these industries is included in order to augment any process and environmental related descriptions. More complete descriptions of phosphate mining and production of "wet process" phosphoric acid are available in a companion guidelines document (USEPA 1980).

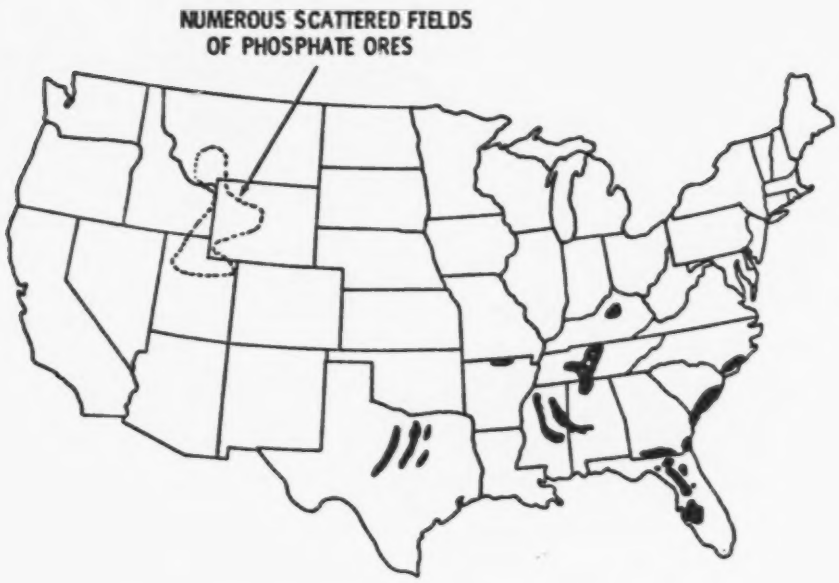
1.2.2.1 Phosphate Rock Mining and Processing

The phosphate mining industry is not a part of the fertilizer or non-fertilizer phosphate industries. Since most phosphate rock mined is used for production of fertilizer and other phosphate products, rather than being exported in raw form, most mining operations include phosphate processing in their corporate activities. For example, of 34 major phosphate industry operations in central Florida, 18 perform processing of phosphate fertilizer or animal feed grade products (USEPA 1978a). Following is a brief description of phosphate mining operations to provide the reader with an idea of the most common procedures.

After any prospecting and mining claims are complete, the mining operation concentrates on matrix or ore extraction and beneficiation of the ore. Extraction of the matrix or ore is done by different processes depending on the location and characteristics of the deposits. Figure 17 is a map showing the locations of the major phosphate deposits in the United States. Ore is actually mined in only four areas - Florida, North Carolina, Tennessee, and several contiguous western states. The mineral content of the phosphate rock varies considerably depending on the location and grade of the rock being mined. Representative analysis of rock from several mining areas is given in Table 2.

In Florida, which accounts for roughly 78% of the United States production of phosphate rock, deposits are alluvial. The phosphate-rich beds are composed of a loosely consolidated conglomerate of phosphate pebbles and clays, known as matrix. The thin overburden deposits are unconsolidated sediments. Mining is conducted by stripping overburden from the matrix deposits by use of electrically driven "walking draglines" equipped with buckets of 20 to 65 cubic yard capacities and booms of 165 to 275 feet in length (USEPA 1978a). In successive moves of the draglines, matrix is removed and

Figure 17. Location of major phosphate rock deposits in the United States.



Source: US Environmental Protection Agency. 1979d. Source assessment, phosphate fertilizer industry. Office of Energy, Minerals, and Industry, Research Triangle Park NC. Prepared by Monsanto Research Corporation, Dayton OH, 186 p.

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Table 2. Representative analysis of commercial phosphate rock.

Component	Location and Type							
	Florida			Tennessee			Western States	
	High Grade Land Pebble	Furnace Grade Land Pebble	Hard Rock High Grade	Hard Rock Waste Pond	Brown Rock High Grade	Brown Rock Furnace Grade	High Grade Phosphate Rock	Low Grade Phosphate Rock
P_2O_5	35.5	30.5	35.3	23.0	34.4	21.2	32.2	19.0
CaO	48.8	46.0	50.2	28.5	49.2	29.1	46.0	23.3
MgO	0.04	0.4	0.03	0.4	0.02	0.6	0.2	1.4
Al_2O_3	0.9	1.5	1.2	14.8	1.2	10.0	1.0	5.9
Fe_2O_3	0.7	1.9	0.9	2.9	2.5	6.2	0.8	4.0
SiO_2	6.4	8.7	4.3	19.8	5.9	25.6	7.5	27.4
SO_3	2.4	2.6	0.1	0.01	0.7	0.4	1.7	1.9
F	4.0	3.7	3.8	2.1	3.8	2.2	3.4	1.8
Cl	0.01	0.01	0.005	0.005	0.01		0.02	
CO_2	1.7	4.0	2.8	1.4	2.0	1.2	2.1	4.0
Org. Carbon	0.3	0.5	0.3	0.3	0.2	0.3	1.8	5.0
Na_2O	0.07	0.1	0.4	0.1	0.2	0.3	0.5	1.5
K_2O	0.09	0.1	0.3	0.4	0.3	0.4	0.4	1.0
H_2O	0.09	0.1	0.3	0.4	0.3	2.4	0.4	2.5
ZnO	1.8	2.0	2.0	7.0	1.4	2.5	2.5	3.5

Source: US Environmental Protection Agency. 1976e. (Draft) Air pollution emissions and control from the manufacture of elemental phosphorus. Industrial Environmental Research Laboratory, Office of Research and Development, Edison NJ, 32 p.

spoil from succeeding cuts is sidecast. As the ore is removed it is stacked in a sluice pit where hydraulic monitors (high-pressure water guns) slurry the ore into pumps for transport by pipeline to the washing plant (USEPA 1978a).

In North Carolina the process is basically the same. The North Carolina deposits occur in interbedded phosphatic clays, limestones, and sands (USEPA 1971b). Hydraulic sluicing and transport are also used in North Carolina where, as in Florida, level terrain and excellent pumping characteristics make these methods feasible.

In Tennessee, the high grade brown rock deposits are a weathered phosphatic limestone that occurs in a north-south belt across the State (Figure 17). Deposits are concentrated in small pockets of phosphate sands surrounded by silica sands. Mining is done by open pit methods. In Tennessee (and the western states also), however, overburden is removed well in advance of actual mining operations (USEPA 1974a). Draglines and small power shovels are used to mine the phosphate sand, which is hauled by truck or rail to the processing plant. Much of the phosphate rock used to make elemental phosphorus is low grade ore from Tennessee and the western states.

The phosphate deposits which are mined in the western states of Idaho, Montana, Wyoming, and Utah account for 14% of United States production (Harre 1976). Western deposits are "hard rock" (consolidated) layers, with degree of hardness generally decreasing the farther north the location. Conventional earth moving equipment is used to remove 5 to 50 feet of overburden. In Utah, the hard rock must be blasted with dynamite. In softer rock areas, "rippers" are used, which are toothed machines that gouge and break the rock from the surface. In Montana, two small underground mines are operated using the room-and-pillar method, which is a kind of underground quarrying. Western rock is usually transported by rail to processing plants.

Beneficiation is the upgrading of the ore by application of processes to the mined matrix or ore to remove inert materials (such as silica sand) or extremely fine materials that cannot be economically separated. Beneficiation processes in Florida and North Carolina vary from plant to plant, depending on grade, size, and ratio of pebbles to fines. A generalized procedure starts

with washing. The matrix slurry (20% to 50% solids) is passed through a series of screens, mills, and washers which break down the matrix to separate phosphate-bearing pebbles from sand and clays. Coarse screening obtains a first fraction of oversize phosphate ore. Further processing of the remaining matrix is done by cyclones to remove very fine sands and colloidal size materials. These are pumped to settling ponds and the remaining fraction undergoes a series of flotations (with tailings going to settling ponds) and finally the ore is dried. Some ore is ground and stored in silos, from which it is transferred to railroad hopper cars for transport (USEPA 1978b).

Tennessee ores are beneficiated by a similar process, except that all water is added at the beneficiation plant since matrix is received dry, and cyclones are operated in a water medium rather than air. A further step for most Tennessee ore is nodulizing in kilns, which prepares the ore for use in electric arc furnaces for production of elemental phosphorus (USEPA 1978o).

Western ore beneficiation starts with crushing and/or scrubbing. Subsequent sizing is done by further crushing, grinding, and size classification. Very fine and colloidal size materials are discharged to a slime pond or thickened for storage as a solid waste. The product is dried or may be calcined before shipment as a product.

Calcining is an operation done on some phosphate rock such as that from the west which has a high organic content or which will be used in processes requiring a higher phosphate content. The rock is subjected to temperatures of 650°-975° C (1202°-1787° F) in rotary drum calcining units (USEPA 1978a). Organics are destroyed and tramp iron materials are removed magnetically. Because of the high energy demands of calcining, it is not done as routinely as it was in the past. Alternate methods can be used in some cases to remove impurities in later processes.

The product of the above processes, ground beneficiated phosphate rock or concentrate, is the raw material for a number of basic fertilizer and phosphorus chemical processes. Additional grinding may be performed after transport, or farther along in the plant complex. The beneficiation process produces slurry effluents that have caused notorious pollution problems in the past in

the form of phosphatic clay slurries, or slime ponds. The magnitude of the disposal problem is indicated by the fact that approximately one ton of slimes (dry weight) is produced per ton of beneficiated phosphate rock (USEPA 1977a). Just one of the larger mining operations in Florida produces 111.4 billion gallons per year of slimes, with up to 45% by weight 0.5 microns in size. These slimes are typically on 5% solids by weight (Hocking 1978). Florida slimes are usually about 70% water after 15 or more years' dewatering and therefore occupy more volume than the original matrix from which they were derived (White et al. 1978). This constitutes one of the phosphate industry's major pollution problems.

1.2.2.2 Production of "Wet Process" Phosphoric Acid

The products of the last two subcategories of the non-fertilizer phosphate industry, defluorinated phosphoric acid and sodium phosphates, are not derived from elemental phosphorus as are the products of the first three. These products are made from or with one of the major intermediate products of the fertilizer industry, "wet process" phosphoric acid. "Wet process" acid is also used in other subcategories of the non-fertilizer phosphate industry, such as in the production of animal feed grade calcium phosphates and defluorination of phosphate rock. Consequently, these processes share some common technology and pollution problems with the fertilizer industry. Therefore, a brief discussion of the production of "wet process" phosphoric acid is presented to give the reader a complete picture of the industry. The reader is referred to the Environmental Impact Assessment Guidelines for New Source Phosphate Fertilizer Manufacturing Facilities for a more detailed description of the processes and environmental problems associated with "wet process" phosphoric acid.

Phosphoric acid is the most important intermediate manufactured by the phosphate fertilizer industry because it is a basic ingredient in every phosphate fertilizer product of the industry other than normal superphosphate and salable phosphate rock. "Wet process" acid, also known as "merchant grade" phosphoric acid, contains more impurities than does "dry process" acid since it is made directly from the phosphate rock. All phosphate fertilizer production from phosphoric acid in the United States uses "wet process" acid.

The "wet process" is based on reaction of phosphate rock with a suitable strong acid to produce phosphoric acid and an acid salt. Sulfuric acid is by far the most widely used acid in the United States for manufacture of phosphoric acid (USEPA 1974a).

A flowsheet typical of the "wet process" for production of phosphoric acid is shown in Figure 18. Ground beneficiated or concentrated phosphate rock is fed continuously to a reaction system where it is mixed with sulfuric acid. The sulfuric acid is diluted, sometimes with contaminated process water, to a proper strength. Then, depending on process temperature and phosphate rock composition, the process is operated to ensure optimal dihydrate crystallization. Some commercial processes also recycle some dilute phosphoric acid into the reaction system. Older plants may have one or more digestion or attack tanks, but in more recent installations the reaction system is a single, large compartmented tank. In this attack vessel, the rock and acid react to form gypsum ($CaSO_4$) and phosphoric acid (H_3PO_4).

To obtain complete reaction, the rock-gypsum-acid slurry is recirculated through the reaction vessel compartments. The reaction is carried out at 75° C for 3-8 hours depending on the particular process being used. Commercial processes typically achieve 96+% efficiencies in extraction of P_2O_5 from rock. The slurry flows from the reactor to a filter where the gypsum is removed and the phosphoric acid is separated into two streams. One stream containing 30-32% P_2O_5 is taken off as the product while a weaker 20% P_2O_5 stream is recycled to the reactor.

Major emissions, effluents, and solid wastes from "wet" phosphoric acid production are hydrogen fluoride gas, sulfur oxides, particulates, acid mists, contaminated cooling and scrubber water, and gypsum solids.

1.3 SIGNIFICANT ENVIRONMENTAL PROBLEMS

This section is an overview of the most significant environmental problems associated with the non-fertilizer phosphate industry. For any particular plant or subcategory some or all of these problems may be anticipated depending on the processes employed and the product line produced. It is

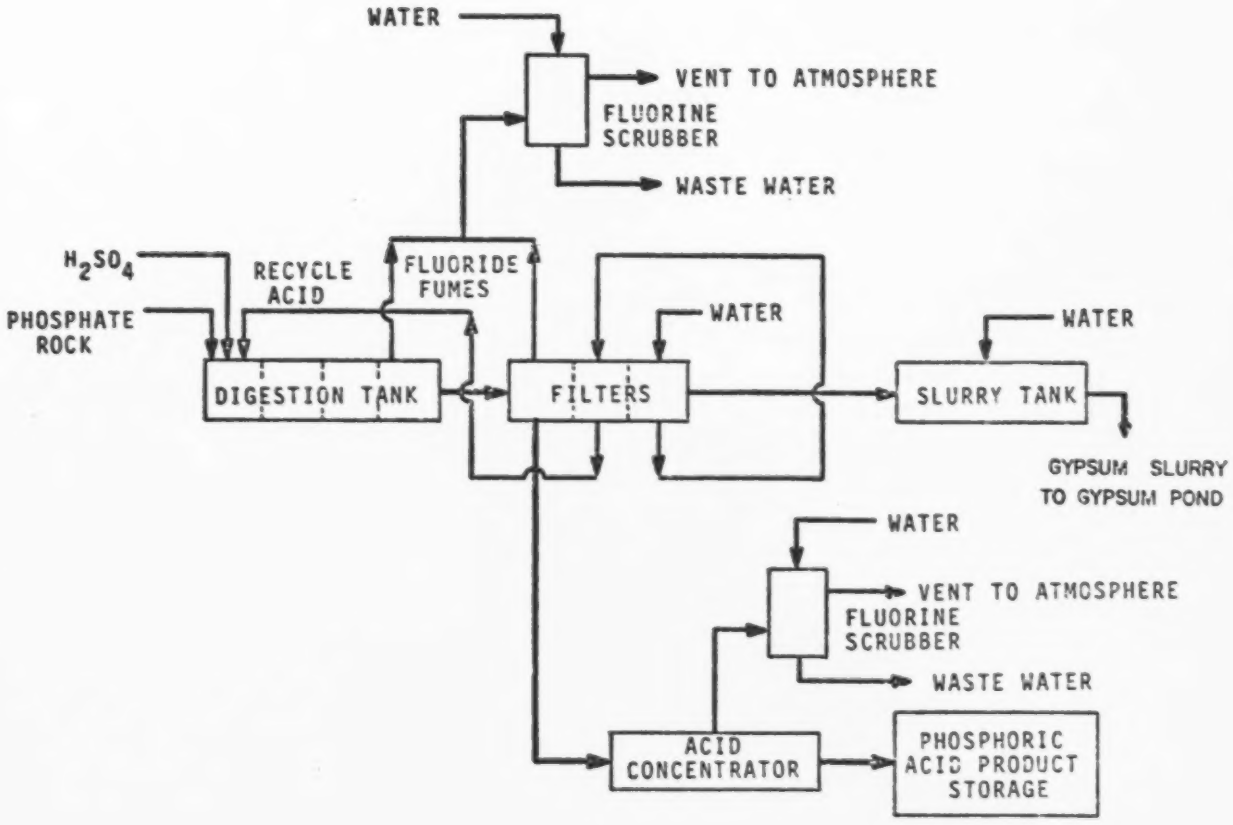

Figure 18. Standard process flow diagram for the manufacture of "wet process" phosphoric acid.

Source: US Environmental Protection Agency. 1971b. Inorganic fertilizer and phosphate mining industries, water pollution and control. Prepared by Battelle Memorial Institute, Richland WA, 225 p.

emphasized that the problems discussed are the most significant, but not necessarily the only problems associated with the industry. A more comprehensive treatment of industry impacts is developed in Section 2.0.

1.3.1 Location

Due to the economic structure of the industry, locational impacts have been minimized. Segments of the industry which require the use of bulk raw materials and generate significant quantities of pollutants have traditionally been located near rural mine sites, while the producers of refined products have been located near the more populated market areas. The relative isolation of phosphorus producers has prevented their sizable emissions of fluorides and particulates from severely affecting ambient air quality in populated areas but problems could develop if a plant were located in a highly populated area with numerous other industries which also have large quantities of emissions.

Some of the potential water quality impacts of a new source phosphate facility are closely related to the rainfall, soils, and groundwater features of the plant location. For defluorination plants, the ratio of rainfall to evaporation is of concern in the maintenance of the water balance between the plant and the recycle pond. Rainfall is also of concern for other plants which practice retention or retention and treatment of contaminated runoff. Also of interest to producers using recycle or retention ponds is the suitability of the soil and subsurface geology for construction and maintenance of dams around the recycle ponds. Unstable soils, steep topography, high groundwater tables, or porous soils overlying a vulnerable source of potable groundwater may limit the capacity of the plant to control its wastewater problems.

1.3.2 Raw Materials

Phosphate Rock

Beneficiated phosphate rock is the primary raw material used by the industry. The mining, beneficiation, and transportation of phosphate rock can have significant impacts on the mining area due to the sheer magnitude of the

operation. Beneficiated rock has generated serious environmental problems in poorly controlled facilities. Dust can be a significant air contamination problem at each point of transfer of the materials and in the grinding process when dry grinding is used. Beneficiation of the phosphate rock also leads to the production of large volumes of clay slimes which are very difficult to dewater and may require large areas of land for storage. Mining impacts are highlighted in Environmental Impact Guidelines for New Source Phosphate Fertilizer Manufacturing Facilities.

Energy

Approximately 12,500 kwh of electricity and 12,000 ft^3 of natural gas are required to produce one ton of elemental phosphorus (USEPA 1973b). Smaller but still significant energy requirements are associated with defluorination of phosphate rock by calcination. This process requires as much as 5,000 ft^3 of natural gas per ton of defluorinated rock (USEPA 1974b). The energy requirements of such manufacturing operations may not be significant in terms of regional supplies but they could have a significant impact on the energy resources of smaller communities.

1.3.3 Process Related Problems

Phossy Water

Water contaminated with colloidal phosphorus (phossy water) from condensation of furnace off-gas or use as an air seal in storage tanks presents difficult problems for producers and consumers of elemental phosphorus, because it is toxic, highly reactive, and not amenable to treatment. Therefore, systems for its segregation, recycle, and reuse are required wherever phossy water is encountered. See Section 2.1.2.1 for a more detailed explanation of this problem.

Fluorine

Significant gaseous emissions of fluorine and fluorine compounds are evolved in the manufacture of phosphorus, defluorinated phosphate rock, and

defluorinated phosphoric acid. Fluorides are transferred from the emission stream to the wastewater and solid waste streams by pollution control equipment. Large quantities are also found in the slag from phosphorus furnaces.

Dust and Particulates

Handling of bulk raw materials and products such as phosphate rock, silica, calcium phosphates, and sodium phosphates creates problems with fugitive dust around the plant site and transshipment areas. Particulates are also generated by many of the industry's production processes and are difficult to control. Calciners, kilns, phosphorus furnaces, and dryers are the most significant particulate sources.

Priority and Toxic Pollutants

Relatively large quantities of fluoride and small quantities of arsenic, cadmium, chromium, zinc, vanadium, uranium, radium 226, radon 222, and other trace elements are present in phosphate rock. These substances may appear in varying concentrations in emissions, wastewater streams, solid wastes, and in unrefined products. Most of these substances are found in small quantities and do not appear to be of significance; however, arsenic, uranium, and radium present special problems and make certain waste streams hazardous. Arsenic is carried through the thermal reduction process and concentrates in the refined phosphorus product. It must be removed during production of many phosphorus derrived products such as sodium phosphates, calcium phosphates and many of the anhydrous derivatives used for food and manufacturing purposes. Arsenic is generally found as waste precipitates or residues from these processes; consequently, these residues require special handling. Unlike arsenic, most of the other contaminants remain in the slag. Due to the low level radiation, phosphorus furnace slag is now considered a hazardous waste under RCRA and must be handled accordingly.

Fluorides are present in large quantities in phosphate rock and are a component of every waste stream. These compounds have not been demonstrated to have an impact on public health and are considered welfare related pollutants which must be controlled but are not generally considered hazardous.

However, toxic fluoride compounds such as calcium fluoride from the cooling/recirculation/scrubber pond may require special handling and disposal if isolated.

Products

Several products of the industry are dangerous by their very nature and are very carefully controlled by plant personnel due to fire, explosive, and poisoning hazards. Both phosphorus and ferrophosphorus present potential fire hazards. Phosphorus must be kept under a water blanket and ferrophosphorus must be kept away from water to prevent explosion. As an indication of its dangerous nature, white phosphorus is used in the manufacture of certain incendiary munitions for the military.

Congress recently appropriated $3.15 million to begin construction of a binary weapons plant at Pine Bluff, Arkansas. The weapons to be produced there include two phosphorus based nerve gases referred to as GB and VX (Barber 1980b). Obviously these products are extremely dangerous and require maximum security precautions.

1.3.4 Pollution Control

The major waste streams and associated pollutants from each subcategory of the industry are identified in Tables 3-8. Most process emissions from the industry are captured by air pollution control equipment, transferred to the wastewater stream, and eventually precipitated to form a solid waste. Properly controlled and contained, these pollutants present only minor problems but poor maintenance, equipment failure, and poor housekeeping may result in their release into the environment. The results of such problems can be relatively low level or major catastrophic events. The lack of equipment maintenance, build up of dust in the vent system, or the inadequate control and entrainment of bulk materials may result in small increases in the emission of particulates and fluorides or runoff of finely divided raw materials and products such as calcium phosphates which are scattered around a plant site. On the other hand, the lack of maintenance in combination with other factors such as poor design or extraordinary rainfall could contribute to the catastrophic failure

Table 3. Major waste streams of the phosphorus production subcategory.

Process	Waste Stream	Significant Pollutants
Furnace charge preparation	Combustion gases from dryers, sintering grate nodulizing, and calcining kilns; Vent gas from travelling grates; Solids material handling cast from combustion gases; Byproduct CO gas flares.	Phosphate dust Coke dust Silica rock dust P_2O_5 Fluorides SO_2
Electrothermal reduction	Handling, proportioning, and feeding of solid materials; Furnace gases escaping through feed bins; Furnace gas leakages; Byproduct CO gas flares; Slag and ferrophosphorus tapping; Solidified slag.	Fluorides Radium 226 P_2O_5 CO Phosphate dust Coke dust Silica rock dust
Product recovery	Condenser exhaust gas; Precipitator dust; Phosphorus and phosphorus sludge storage; Phosphorus sludge cleaning; Water contaminated with elemental phosphorus; Slag crushing and handling.	Elemental phosphorus Nutrients P_2O_5 Lower oxides of phosphorus Fluorides Fluosilicates

Source: Barber, J.C. 1980b. Comments on document, "Environmental Impact Assessment Guidelines for New Source Non-Fertilizer Phosphate Manufacturing Facilities."

Table 4. Major waste streams of the phosphorus consuming subcategory.

Product	Waste Stream	Significant Pollutants
Phosphoric Acid	Phosphorus handling	Phosphorus (phossy) water
	Combustion gases	Acid mist (H_3PO_4)
	Filter solids	*Arsenic sulfide
Phosphorus Pentoxide	Phosphorus handling	Phosphorus (phossy) water
Phosphorus Pentasulfide	Phosphorus handling	Phosphorus (phossy) water
	Distillation residues	*Arsenic pentasulfide
	Casting fumes	SO_2, P_2O_5
Phosphorus Trichloride	Phosphorus handling	Phosphorus (phossy) water
	Distillation residues	*Arsenic trichloride
	Distillation vapors	PCl_3
Phosphorus Oxychloride	Distillation vapors	HCl, H_3PO_4

* Very small quantities generated.

Source: U.S. Environmental Protection Agency. 1973a. Development document for proposed effluent limitations guidelines and new source performance standards for the phosphorus derived chemicals segment of the phosphate manufacturing point source category. Office of Air and Water Programs, Washington DC, 159 p.

Table 5. Major waste streams of the phosphate chemicals subcategory.

Process	Waste Stream	Significant Pollutants
Sodium tripolyphosphate manufacture	White mud drying/ calcination emissions	Silica, iron, aluminum phosphates, particulates
Calcium phosphates manufacture	Filtrate from dicalcium phosphate dewatering	Calcium phosphates
	Drying emissions	Particulates, phosphates

Source: U.S. Environmental Protection Agency. 1973a. Development document for proposed effluent limitations guidelines and new source performance standards for the phosphorus-derived chemicals segment of the phosphate manufacturing point source category. Office of Air and Water Programs, Washington DC, 159 p.

Table 6. Major waste streams of the defluorinated phosphate rock subcategory.

Process	Waste Stream	Significant Pollutants
Raw material handling	Fugitive dust	Dust
Calcination	Effluent gases from reactor and furnace firing	Fluorine SO_2 particulates
Quenching	Quenching water	Phosphates, fluoride trace pollutants.

Source: US Environmental Protection Agency. 1976a. Development document for effluent iimitations guidelines and new source performance standards for the other non-fertilizer phosphate chemicals segment of the phosphate manufacturing point source category. Office of Water and Hazardous Materials, Washington DC, 105 p.

Table 7. Major waste streams of the defluorinated phosphoric acid subcategory.

Process	Waste Stream	Significant Pollutants
Vacuum evaporation	Evaporator gas stream	Acid mist, fluorides
	acid mist	fluorides, phosphates, metals
	condenser water	fluorides
Submerged combustion	Fuel combustion products	SO_2
	product gas stream	Silicon tetrafluoride, hydrogen fluoride, acid mists
Aeration	Process emissions	Tetrafluosilene

Source: US Environmental Protection Agency. 1976a. Development document for effluent limitations guidelines and new source performance standards for the other non-fertilizer phosphate chemicals segment of the phosphate manufacturing point source category. Office of Water and Hazardous Materials, Washington DC, 105 p.

Table 8. Major waste streams of the sodium phosphate subcategory.

Process	Waste Stream	Significant Pollutants
Calcination of phosphate rock	Emissions	Fluorine Particulates SO_2
Acidulation	Emissions Solid waste	Acid mist Gypsum
Precipitation/ Filtration	Solid waste	Arsenic sulfide
Neutralization	Solid waste	Iron & aluminum Phosphates

Source: US Environmental Protection Agency. 1976a. Development document for effluent limitations guidelines and new source performance standards for the other non-fertilizer phosphate chemicals segment of the phosphate manufacturing point source category. Office of Water and Hazardous Materials, Washington DC, 105 p.

of a recirculation pond dam and the release of its highly polluted contents. The process wastewater in these ponds has a low pH (less than 2.0) and contains the entire range of pollutants generated by the industry. Even without failure, seepage around a dam structure can introduce smaller quantities of the same pollutants into receiving waters. Maintenance of such structures should be carefully monitored.

1.4 TRENDS

Trends in the non-fertilizer phosphate industry are difficult to identify. The industry is highly fragmented consisting of several individual groups of producers whose products and processes are relatively unrelated except for the principal material, phosphate. Portions of this industry such as defluorinated acid are more closely related to the fertilizer industry than to other non-fertilizer phosphate segments, which creates a problem in obtaining unified projections. Finally, because non-fertilizer phosphate manufacture is not a growth industry its trends are slow to develop and obscured by the trends of the phosphate industry as a whole.

1.4.1 Markets and Demands

Overall the phosphate industry produces a variety of intermediate products for the agriculture, chemical, and food industries. As indicated in Figure 19, approximately 82.6% (total agricultural use less defluorinated rock) of phosphate rock consumed in the United States during 1975 was used for fertilizer production, while only 17.4% was used for non-fertilizer purposes. For the non-fertilizer phosphate segment of the industry, the largest product is furnace grade or "dry process" phosphoric acid which is used for the manufacture of food additives (calcium phosphates) and household detergents (sodium phosphates). Of the estimated 460,000 tons of phosphorus produced in 1979, approximately 85% was used for production of furnace acid, while only 10% was used for other products (Chemical and Engineering News 1980).

Unified forecasts of markets and demands for non-fertilizer phosphate chemicals are incomplete at best. Growth forecasts for SIC 2819 (Industrial Inorganic Chemicals, n.e.c.), which includes most segments of the industry,

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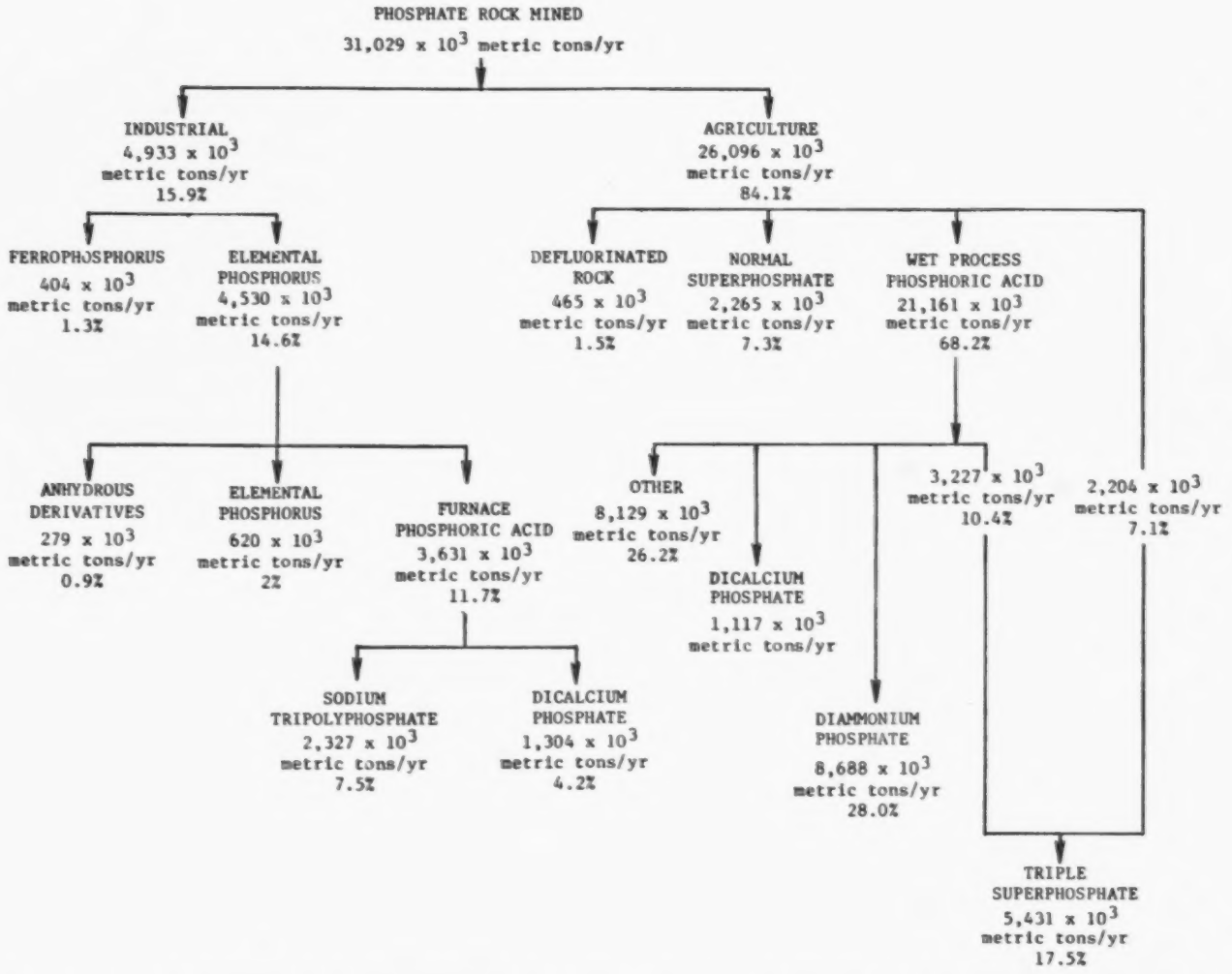
Figure 19. 1975 phosphate rock consumption pattern for various phosphorus products.



Source: US Environmental Protection Agency. 1979d. Source assessment, phosphate fertilizer industry. Office of Energy, Minerals and Industry, Research Triangle Park NC. Prepared by Monsanto Research Corporation, Dayton OH, 186 p.

indicate a 3.5% compound annual rate of real growth to 1984 (U.S. Dept. of Commerce 1980). An examination of recent production trends for elemental phosphorus, cadmium phosphate, and phosphorus trichloride, (Table 9) indicates a slow, steady rate of growth for the industry. Production of sodium tripolyphosphate declined during the 1970's due to environmental concerns over the use of phosphate detergent.

Projections of phosphate rock demand by end use for the year 2000, prepared for the U.S. Bureau of Mines (Stowasser 1977), also forecast slow growth rates for most segments of the industry (Table 10). Based on these projections, phosphate chemicals made for use in detergents will remain at present levels of production. Non-phosphate chemicals such as alumino-silicates, sodium nitrilotriacetate, and sodium nitrates are being examined as potential replacements for phosphate based detergent building. However, these substitutes are plagued with problems of higher cost, lower effectiveness, or a greater possibility for irritation (USDOC 1980). Phosphate chemicals manufactured for animal feed (defluorinated phosphate rock, dicalcium phosphate, etc.) should increase by approximately 85% over 1975 levels by the year 2000. The production of food grade phosphate chemicals are projected nearly to double by 2000. These forecasts were based on several assumptions: 1) reduced phosphorus content in detergents will be compensated by the growth in detergent demand; and 2) both animal feed and food-grade phosphorus products will increase in demand proportionally to population forecasts.

Foreign trade in non-fertilizer phosphate chemicals is quite small. In 1979 an estimated 171,436 short tons of phosphorus, calcium phosphates, sodium tripolyphosphates, and other sodium phosphates valued at $88.6 million were exported to foreign markets, which represents a small fraction (8%) of domestic production. Most of the major industrialized countries, and some of the developing nations, prefer to import the basic mineral products for processing within their countries instead of importing finished products (USDOC 1980).

In summary, the future production levels of the various subcategories of the non-fertilizer phosphate chemical industry, with the exception of sodium tripolyphosphate, should increase at a slow, steady pace. Sodium tripolyphosphate, on the other hand, will level out at current levels of production into the forseeable future.

Table 9. Production of selected non-fertilizer phosphate chemicals, 1973-1979 (quantity in 1,000 short tons, 100% basis).

	1973	1974	1975	1976	1977	1978	1979[1]
Elemental phosphorus	526	524	450	437	431	441	460
Calcium phosphate	540	611	522	656	699	766	817
Phosphorus trichloride	80	75	82	83	95	100	115
Sodium tripolyphosphate	967	903	770	724	717	735	750

[1] Estimated

Source: U.S. Department of Commerce. 1980. 1980 U.S. industrial outlook for 200 industries with projections for 1984. US Government Printing Office, Washington DC, 515 p.

Table 10. Projections and forecasts for U.S. phosphates rock demand by end use, 1975-2000 (thousand short tons).

		2000		
End Use	1975	Low	High	Probable
Detergents	3,212	3,200	3,200	3,200
Animal grade feed	1,539	2,400	3,400	2,800
Food products	273	400	600	500

Source: Adapted from Stowasser, W.F. 1977. Phosphate rock, the present and future supply and demand. Letter from U.S. Bureau of Mines and R.E. McNeill, US Environmental Protection Agency, Region IV.

1.4.2 Locational Changes

The distribution of non-fertilizer phosphate chemical plants is indicated in Table 11 by industry subcategory and by state. Florida, the nation's leading producer of phosphate rock, contains the largest number of plants, some of which are associated with the phosphate fertilizer industry.

Two predominate siting or locational patterns can be identified within the industry. Facilities in the Phosphorus Production and Defluorinated Phosphate Rock subcategories tend to locate relatively near to the source of phosphate rock, which is mined in Florida, Idaho, Montana, North Carolina, and Tennessee. Because these industries use large quantities of phosphate as a raw material, transportation costs make it economically prohibitive to locate these facilities elsewhere. The remaining four subcategory industry types tend to locate closer to their market area. As an example, almost all of the STPP (sodium tripolyphosphate) plants in the United States are located near specific detergent manufacturing plants, the primary market for STPP (USEPA 1973b).

With some exceptions, new source non-fertilizer phosphate plants can be expected to follow the existing locational trends discussed above. A potential exception to this is the relocation of several Tennessee phosphorus producers to other phosphate mining locations. Projections indicate that production of phosphate rock in Tennessee will terminate and force the relocation or permanant shutdown of that portion of the industry's phosphorus production capacity (Stowasser 1977). Within the near future, however, the likelihood of new production facilities is slim.

1.4.3 Trends in Raw Materials

The basic raw materials utilized in the various subcategories of the non-fertilizer phosphate industry include phosphate rock, coke, silica, electric energy, elemental phosphorus, dry process phosphoric acid, and wet process phosphoric acid. The important trends pertaining to these raw materials are discussed below:

Table 11. Locational distribution of non-fertilizer phosphate chemical plants in the United States.

	CA	FL	GA	IA	ID	IL	IN	KS	LA	MI	MO	MT	NE	NJ	NY	NC	OH	PA	SC	TN	TX	VT	WY	WV
Phosphorus Production		2			2							1								3				
Phosphorus Consuming	4																							
Phosphate																								
Defluorinated Rock																								
Def. Acid																								
Sodium Phosphate																								

Sources: US Environmental Protection Agency. 1973a. Development document for proposed effluent limitations guidelines and new source performance standards for the phosphorus-derived chemicals segment of the phosphate manufacturing point source category. Office of Air and Water Programs, Washington DC, 159 p.

US Environmental Protection Agency. 1976a. Development document for effluent limitations guidelines and new source performance standards for the other non-fertilizer phosphate chemicals segment of the phosphate manufacturing point source category. Office of Water and Hazardous Materials, Washington DC, 105 p.

Revised per Barber 1980

Phosphate Rock - the supply of domestically produced phosphate rock is projected to increase until the year 2000 and then gradually decline. The quality (P_2O_5 content) of domestic rock supplies will also decline as the existing high-quality deposits are depleted (USEPA 1980).

Coke - the supply of metallurgical coke is inadequate. Some phosphorus porducers use reformed coke and petroleum coke in addition to metallurgical coke as a reducing carbon. Low-volatile bituminous coal is also being considered as a reducing carbon (Barber 1980b).

Silica - no changes in silica availability and use have been identified. This mineral is easily obtained by the industry.

Elemental Phosphorus - produced within the industry, elemental phosphorus is also a raw material for the phosphorus consuming subcategory. From 1978 to 1980, the price of elemental phosphorus has increased by approximately 9% (Barber 1980a). Electric furnaces for phosphorus production are increasing in size to achieve operating economies (USEPA 1973a).

"Dry Process" Phosphoric Acid - used as the raw material in most detergent and food grade phosphates, this acid is increasing in price as the cost of elemental phosphorus and energy increases. Additional production of the acid may depend on the benefits of using highly concentrated (76% P_2O_5) acid for making fertilizers (Barber 1980b). This highly concentrated acid can be made from dry process phosphoric acid whereas the maximum concentration that can be achieved from merchant-grade, "wet process" acid is around 70% P_2O_5.

"Wet Process" Phosphoric Acid - no new production trends have been identified for this product which is used in the production of defluorinated phosphoric acid and some sodium phosphates. However, a shortage of sulfur, a basic raw material, may drive the price of wet process acid up during the coming years (Giusti 1980).

Electric Energy - used to produce elemental phosphorus, the price of electric energy has increased by 377% through the seventies (Barber 1980a). High energy costs have forced the elemental phosphorus industry to shut down smaller furnaces as a retrenchment step and switch production to the larger, more efficient furnaces (USEPA 1973a).

1.4.4 Process Trends

Processes in predominant use by non-fertilizer phosphate producers are described in Section 1.2. Following are highlights of processes which have been tried by the industry and appear to be gaining favor. There is also a possibility of increasing crossover technology from the larger and faster growing phosphate fertilizer industry affecting the processes implemented in non-fertilizer phosphate facilities.

- Phosphorus production facilities have been built using progressively larger furnaces to achieve a greater economy of scale. The average furnace production of 15,000 tons of phosphorus/year in 1950 grew to 40,000 tons/year by 1970 (USEPA 1973a).
- Recycled "dry process" phosphoric acid from the product line and acid mist control facilities can be used in the hydrator to obtain more concentrated acid with less water use (USEPA 1973a).
- Defluorination of phosphate rock is accomplished more rapidly and at lower temperature using a fluid bed reactor rather than a rotary kiln. The use of fluid bed reactors is a long established trend and is widely accepted in the industry (USEPA 1976a).
- Defluorinated phosphoric acid is produced largely by the fertilizer industry as superphosphoric acid. The preferred process in the fertilizer industry is vacuum evaporation due to its reduced tail gas scrubbing requirements. Non-evaporative defluorination of phosphoric acid using silica addition and aeration stripping may offer advantages in the future due to lower energy requirements (USEPA 1976a).

1.4.5 Pollution Control Trends

Pollution control systems applicable to the industry are described in Section 3.0. Following are highlights of pollution control technologies which have been successfully implemented by the non-fertilizer phosphate industry and appear to be gaining favor among producers. Also included are potential crossover technologies that have been adopted by the fertilizer industry and may also be applicable to similar situations in the non-fertilizer phosphate industry.

Treatment of final wastewater effluents is a relatively small segment of the total pollution control effort of most plants because of the no discharge

requirements placed on much of the industry. Housekeeping and operational and design controls are the basis of an effective wastewater management program and require the most emphasis if stringent pollution control requirements are to be met. Internal water management control techniques may include:

- Prevention of cooling water contamination from contact with process waste by prompt repair of leaks and equipment.
- Recycle and reuse of scrubber water after appropriate treatment.
- Containment of all spills and leaks by the use of dikes, pumps, and catch basins.
- Reuse and recycle of phossy water.
- Containment and treatment of all contaminated runoff from specified rainfall events by routing to the recirculation pond.
- Management of the overall plant water balance by integrated control of plant processes.
- Recirculation of seepage from ponds.
- Prevention of pollutant introduction to wastewater streams by the use of dry dust and particulate collectors such as baghouses.
- If discharge is necessary from recirculation or no-discharge facilities, proper treatment by double liming should be practiced.

Emission control for air-borne pollutants is probably the industry's single most rapidly changing area of technology. Controls which appear to be widely accepted are:

- Cyclones for control of dust and large particulates.
- Baghouses for control of dust and smaller noncarbonaceous particulates. (These may be preceded by a cyclone.)
- Electrostatic precipitators for control of fine particulates.
- Wet scrubbing for control of fumes and combined fine particulate/fume emission streams. Scrubber systems frequently used include:
    1) Venturi scrubbers
    2) Spray towers
    3) Packed bed scrubbers
    4) Cyclonic scrubbers

- Forced air collection hood systems at critical operation points throughout a plant to collect fumes from fugitive sources such as tap holes and slag quenching areas in a phosphorus plant.
- Skirts around dry material transfer and handling systems and dry raw material and product handling locations.

Trends have not yet developed in the handling of the hazardous waste materials of the industry in accordance with the requirements of RCRA; however, rapid advances are expected in the near future.

Solid waste management programs currently in use by the industry include:

- Product recovery or reuse from solid wastes including dust and sludges from air emission control equipment.
- Sale of waste materials such as arsenic trichloride still bottoms for reprocessing.
- Pond storage of fluoride precipitates from emission and wastewater treatment systems.

1.5 REGULATIONS

1.5.1 Water Pollution Control Regulations

The Federal Water Pollution Control Act (FWCA) Amendments of 1972 (P.L. 92-500) established two major interrelated procedures for controlling industrial effluents from new sources, and specifically included phosphate manufacturing in the list of affected categories of sources. The principal mechanism for discharge regulation is the NPDES permit. The other provision is the New Source Performance Standard (NSPS). The Clean Water Act of 1977 (P.L. 95-217), which amends P.L. 92-500, made no change in these basic procedures.

The NPDES permit, authorized by Section 402 of FWPCA, prescribes the conditions under which effluents may be discharged to surface waters. The conditions applicable to new or expanded phosphate manufacturing facilities will also be in accordance with New Source Performance Standards adopted by USEPA pursuant to Section 306, and pretreatment standards promulgated to

implement Section 307(b). Different standards will be applicable depending on the subcategory under consideration. Stricter effluent limitations may be applied on a site-specific basis if required to achieve water quality standards.

The effluent NSPS promulgated for new sources in the Phosphate Manufacturing Point Source Category are listed in Table 12. With the exception of the sodium phosphates subcategory, NSPS promulgated for the non-fertilizer phosphate industry under 40 CFR 422 prohibit discharge of any process wastewater pollutants to navigable waters except under emergency conditions. For the phosphorus-producing, phosphorus-consuming, and phosphate subcategories this limitation is straightforward. For the defluorinated phosphate rock and defluorinated phosphoric acid subcategories, however, the basic no-discharge NSPS limitation must be qualified to reflect the problems associated with maintenance of the critical water balance between the plant and the recirculation pond during extremely wet weather. Recirculation ponds perform an integral part in closed loop wastewater treatment and reuse schemes of most phosphoric acid operations in the fertilizer industry and defluorinated rock and acid operations in the non-fertilizer phosphate industry including cooling and settling of calcium precipatates from treatment of wastewater with lime. The pond typically provides sufficient treatment of process wastewater to allow its resue as makeup water while also providing an evaporative surface and waste flow buffering vessel to keep the operation hydraulically balanced without discharge. Obviously, however, the pond has limited capacity and can be overloaded by an unusually large rainfall. In such an event, provisions must be made for treatment and discharge of recirculation pond effluents to prevent dike overflow and damage to the pond. For this reason there are several lengthy but specific footnotes to Table 12 outlining the conditions under which effluents from the recirculation ponds may be discharged.

New sources that discharge wastewater to publicly owned treatment works (POTW) are required to comply with USEPA's pretreatment regulations, issued in the 26 June 1978, Federal Register (40 CFR 403). These regulations stipulate that certain POTW's categorized by size and influent characteristics, develop POTW Pretreatment Programs. These programs are intended to prevent the intro-

Table 12. Standards of performance for new source wastewater effluents of the non-fertilizer phosphate manufacturing point source category (41 FR 25974, June 23, 1976).

Standards Category		Standards of Performance for New Sources	Pretreatment for New Sources
A.	Phosphorus Production	no discharge of process wastewater pollutants to navigable waters	(Note 2)
B.	Phosphorus Consuming	no discharge of process wastewater pollutants to navigable waters	(Note 2)
C.	Phosphate	no discharge of process wastewater pollutants to navigable waters.	(Note 2)
D.	Defluorinated Phosphate Rock	no discharge of process wastewater (1) pollutants to navigable waters (3)	NA
E.	Defluorinated Phosphoric Acid	no discharge of process wastewater (1) pollutants to navigable waters (3)	NA
F.	Sodium Phosphates	(4)	NA

(1)a The term "process wastewater" means any water which, during manufacturing or processing, comes into direct contact with or results from the production or use of any raw material, intermediate product, finished product, by-product, or waste product. The term "process wastewater" does not include contaminated non-process wastewater, as defined below.

b The term "contaminated non-process wastewater" means any water including precipitation runoff, which during manufacturing or processing, comes into incidental contact with any raw material, intermediate product, finished product, by-product or waste product by means of (1) precipitation runoff, (2) accidental spills, (3) accidental leaks caused by the failure of process equipment and which are repaired or the discharge of pollutants therefrom contained or terminated within the shortest reasonable time which shall not exceed 24 hours after discovery or when discovery should reasonably have been made, whichever is earliest, and (4) discharges from safety equipment, and from equipment washings for the purpose of safe entry, inspection and maintence; provided that all reasonable measures have been taken to prevent, reduce, eliminate and control to the maximum extent feasible such contact and provided further that all reasonable measures have been taken that will mitigate the effects of such contact once it has occurred.

Table 12. Standards of performance for new source wastewater effluents of the non-fertilizer phosphate manufacturing point source category (continued).

c The term "25-year 24-hour rainfall event" means the maximum precipitation event with a probable recurrence interval of once in 25 years as defined by the National Weather Service in Technical Paper No. 40, "Rainfall Frequency Atlas of the United States," May, 1961, and subsequent amendments or equivalent regional or state rainfall probability information developed therefrom (41 FR 25974, June 23, 1976).

(2) Pretreatment standards for new sources in this subcategory revoked by 43 FR 46020, October 5, 1978.

(3) The following standards of performance establish the quantity or quality of pollutants or pollutant properties which may be discharged by a new source subject to the provisions of this subpart: (40 CFR 422.45 422.55)

a Subject to the provisions of paragraphs (b) and (c) of this section, the following limitations establish the quantity or quality of pollutants or pollutant properties, controlled by this section, which may be discharged by a point source subject to the provisions of this subpart after application of standards of performance for new sources: there shall be no discharge of process wastewater pollutants to navigable waters (41 FR 25974, June 23, 1976)

b Process wastewater pollutants from a calcium sulfate storage pile runoff facility operated separately or in combination with a water recirculation system designed, constructed, and operated to maintain a surge capacity equal to the runoff from the 25-year, 24-hour rainfall event (see (1) c above) may be discharged, after treatment to the standards set forth in paragraph (c) below, whenever chronic or catastrophic precipitation events cause the water level to rise into the surge capacity. Process wastewater must be treated and discharged whenever the water level equals or exceeds the midpoint of the surge capacity (41 FR 25974, June 23, 1976).

c The concentration of pollutants discharged in process wastewater pursuant to the limitations of paragraph (b) shall not exceed the values listed in the following table:

Table 12. Standards of performance for new source wastewater effluents of the non-fertilizer phosphate manufacturing point source category (concluded).

Effluent Characteristic	Effluent Limitations (mg/l)	
	Maximum for any one day	Average of daily values for 30 consecutive days shall not exceed
Total Phosphorus (as P)	105	35
Fluoride	75	25
TSS	150	50
pH (standard units)	6-9.5	

(41 FR 25974, June 23, 1976)

(4) Standards of Performance for New Source Manufacturers producing Sodium Phosphates from "Wet Process" Phosphoric Acid, 40 CFR 422.65. The following limitations establish the quantity or quality of pollutants or pollutant properties, controlled by this section, which may be discharged by a point source subject to the provisions of this subpart after application of the standards of performance for new sources:

[Metric units, kg/kkg* of product; English units, lb/1,000 of product]

Effluent Characteristic	Effluent Limitations (mg/l)	
	Maximum for any one day	Average of daily values for 30 consecutive days shall not exceed-
TSS	0.35	0.13
Total Phosphorus (as P)	0.56	0.28
Fluoride (as F)	0.21	0.11
pH	Within the range 6.0 to 9.5.	

(41 FR 25974, June 23 1976)

* kkg = thousand kilograms

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duction of pollutants by industrial users that would interfere with the operation of treatment works, would pass through treatment works, or would adversely affect opportunities to recycle and reclaim wastewaters and sludges.

Regardless of specific limitations required by the Pretreatment Programs, the regulations (40 CFR 403.5) state that the following may not be introduced into a POTW:

- pollutants which create a fire or explosion hazard in the POTW;
- pollutants which will cause corrosive structural damage to the POTW, but in no case discharges with pH lower than 5.0, unless the works is specifically designed to accommodate such discharges;
- solid or viscous pollutants in amounts which cause obstruction to the flow in sewers, or other interference with the operation of the POTW; and
- any pollutant, including oxygen-demanding pollutants, released in a discharge of such volume or strength as to cause interference in the POTW.

In addition, there is a restriction on thermal discharges that became effective in June 1981.

With respect to the phosphate industry, pretreatment standards are not well defined. Pretreatment standards for the first three subcategories dealing with phosphorus-derived chemicals have been revoked as indicated in Table 12. For the latter three subcategories dealing with other non-fertilizer phosphate chemicals, new source pretreatment standards have not be promulgated.

NPDES permits also impose special conditions beyond the effluent limitations stipulated, such as schedules of compliance and treatment standards. Once plants are constructed in conformance with all applicable standards of performance, they are relieved by Section 306(d) from meeting any more stringent standards of performance for 10 years or during the period of depreciation or amortization, whichever ends first. However, this guarantee does not extend to effluent standards for priority pollutants adopted under Section 307(a), which can be added to the processing plant's NPDES permit when they are promulgated. These effluent standards will be promulgated if the finding

is that an industry's effluents contain more than trace amounts of the priority pollutants under investigation by USEPA. A number of priority pollutants are known to be present in phosphate industry wastes including cadmium, chromium, zinc, and arsenic. P.L. 95-217 also expands Section 307(a) of P.L. 92-500 dealing with toxic standards or prohibitions on existing sources. Thus, any evaluation of the impact of new or expanded phosphate plants should include a verification on the status of applicable toxic effluent standards.

Many states have qualified, as permitted by P.L. 92-500, to administer their own NPDES permit programs. The major difference in obtaining an NPDES permit through approved state programs vis-a-vis the Federal NPDES permit program is that the Act does not extend the NEPA environmental impact assessment requirements to state programs. Because over half the States have enacted NEPA-type legislation, it is likely that new plants or major expansions of existing plants will come under increased environmental review in the future. Since the scope of the implementing regulations varies considerably, current information on prevailing requirements should be obtained early in the planning process from permitting authorities in the appropriate jurisdiction.

1.5.2 Air Pollution Control Regulations

New Source Performance Standards (NSPS)

National air pollution performance standards have not yet been promulgated for the non-fertilizer phosphate industry. In the absence of Federal emission standards, air quality impacts are assessed based on ambient air quality standards and applicable state and local standards.

National Ambient Air Quality Standards

National Ambient Air Quality Standards (NAAQS) (40 CFR 50) that specify the minimum ambient air quality that must be maintained in the United States are shown in Table 13. Standards designated as primary are those necessary to protect the public health with an adequate margin of safety, and secondary standards are those necessary to protect the public welfare from any known or anticipated adverse effects of air pollution.

A combined Federal/state regulatory program is designed to achieve the objectives of the Clean Air Act and NAAQS. Each state must adopt and submit to USEPA a State Implementation Plan (SIP) for maintaining and enforcing primary and secondary air quality standards in Air Quality Control Regions. USEPA either approves the state's SIP or proposes and implements an alternate plan. The SIP's contain emission limits which may vary within a state due to local factors such as concentrations of industry and population. Because SIP's have been subject to frequent revision, it is best to verify the status of the SIP requirements before applying them.

There are two alternate programs requiring preconstruction approval of industrial air pollution abatement systems. These are the Prevention of Significant Deterioration (PSD) Program which applies to areas in compliance with NAAQS and the Nonattainment Program for areas which are in violation of NAAQS.

Prevention of Significant Deterioration (PSD)

In 1974 USEPA issued regulations for the PSD Program under the 1970 version of the Clean Air Act (P.L. 90-604). These regulations established a plan for protecting areas that possess air quality which is cleaner than that dictated by the National Ambient Air Quality Standards. The PSD Program components include:

- A classification system for areas of the country meeting NAAQS.
- Limitations on the increase in concentration of pollutants above baseline conditions.
- Best Available Control Technology requirement for large sources.
- Preconstruction review and approval by permit of new source air pollution facility abatement programs.

Under USEPA's PSD regulatory plan, all areas of the nation are designated as one of three classes. The plan permits specified numerical increments of air pollution increases from major stationary sources for each class, up to a level considered to be significant for that area. Class I provides extraordinary protection from air quality deterioration and permits only minor

Table 13. National primary and secondary ambient air quality standards (40 CFR Part 50).

	Type of Standard	Averaging Time	Frequency Parameter	Concentration ug/m^3	Concentration ppm
Carbon monoxide[a]	Primary	1 hr	Daily maximum[a]	40,110	35
		8 hr	Daily maximum[a]	10,310	9
Hydrocarbons[c]	Primary and secondary	3 hr (6 to 9 a.m.)	Annual maximum[b]	160	0.24[c]
Nitrogen dioxide	Primary and secondary	1 yr	Arithmetic mean	100	0.05
Particulate matter[e]	Primary	24 hr	Annual maximum[b]	260	-
		24 hr.	Annual geometric mean	75	-
	Secondary	24 hr	Annual maximum[b]	150	-
		24 hr.	Annual geometric mean	60[d]	-
Sulfur dioxide	Primary	24 hr	Annual maximum[b]	365	0.14
		1 yr	Arithmetic mean	80	0.03
	Secondary	3 hr	Annual maximum[b]	1,300	0.5
Lead	Primary	90 day	Quarterly maximum[c]	1.5	-
Ozone	Primary and secondary	1 hr	Daily maximum[a]	235	0.12

a. Expected exceedence less than or equal to one per year.

b. Not to be exceeded more than once per year.

c. As a guide in devising implementation plans for achieving oxidant standards.

d. As a guide to be used in assessing implementation plans for achieving the annual maximum 24-hour standard.

e. Not to be exceed more than once per 90 days.

Source: Adapted from 40 CFR Part 50, and 45 FR 55065.

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increases in air pollution levels. Under this concept, virtually any increase in air pollution in these pristine areas is considered significant. An exception may be granted to a source exceeding the Class I allowable increase on these mandatory Class I areas if the Federal Land Manager certifies that the facility will have no adverse impact on the air quality-related values of the area, including visibility. Class II increments permit increases in air pollution levels that would accompany well-controlled growth. Class III increments permit increases in air pollution levels up to the NAAQS. Acceptable increases in pollutant concentrations over background for each of the three PSD classes are shown in Table 14.

Sections 160 - 169 were added to the Act by the Clean Air Act Amendments of 1977. These Amendments adopted the basic concept of the above administratively developed procedure of allowing incremental increases in air pollutants by class. Through these Amendments, Congress also provided a mechanism to apply a practical adverse impact test which did not exist in the USEPA regulations previously.

As indicated in Table 14, the PSD requirements of 1974 apply only to two pollutants: total suspended particulates (TSP) and sulfur dioxide (SO_2). However, Section 166 requires USEPA to promulgate PSD regulations which address nitrogen oxides, hydrocarbons, lead, carbon monoxide, and photochemical oxidants, including use of increments or other effective control strategies which, if taken as a whole, accomplish the purposes of PSD policy set forth in Section 160.

The 1977 Amendments designate certain Federal lands as Class I, including all international parks, national memorial parks, national wilderness areas which exceed 5,000 acres, and national parks which exceed 6,000 acres. This constitutes 158 areas which may not be redesignated to another class through state or administrative action. The remaining areas of the country have been initially designated Class II. Within this Class II category, certain Federal lands over 10,000 acres (national primitive areas, national wild and scenic

Table 14. Nondeterioration (PSD) increments for SO_2 and particulate matter in areas with different air quality classifications.

Pollutant	Class I (ug/m^3)	Class II (ug/m^3)	Class III (ug/m^3)	Class I exception (ug/m^3)
Particulate matter:				
Annual geometric mean	5	19	37	19
24-hour maximum	10	37	75	37
Sulfur dioxide:				
Annual arithemetic mean	2	20	40	20
24-hour maximum	5*	91	182	91
3-hour maximum	25*	512	700	325

*A variance may be allowed to exceed each of these increments on 18 days per year, subject to limiting 24-hour increments of 36 ug/m^3 for low terrain and 62 ug/m^3 for high terrain and 3-hour increments of 130 ug/m^3 for low terrain and 221 ug/m^3 for high terrain. To obtain such a variance requires both State and Federal approval.

Source: Public Law 95-95. 1977. Clean Air Act Amendments of 1977, Part C, Subpart 1, Section 163 (Passed August 1977).

rivers, national wildlife refuges, national seashores and lakeshores, and new national park and wilderness areas) established after 7 August 1977 will be Class II "floor areas" ineligible for redesignation to Class III.

The general responsibility for redesignation of PSD areas lies with the states. The Federal land Manager has an advisory role for redesignation to the appropriate state and to Congress. Redesignation by Congress will require the normal legislative process of committee hearings, floor debate, and action. In order for a state to redesignate areas, the detailed process (outlined in Section 164(b) of the 1977 Amendments) would include an analysis of the health, environmental, economic, social, and energy effects of the proposed redesignation which would be discussed at a public hearing.

Federal regulations require that any new source of emissions that obtains its permits after March 1, 1978, or has the potential for production of 250 tons/year (227 kkg) of any registered pollutant, before controls, must undergo full PSD review and receive preconstruction approval. Full PSD review requires analysis of effects of the source on air quality increments, application of Best Available Technology, and a comprehensive monitoring program. Applicants for construction permits must demonstrate by monitoring and submission of air quality data that the new facility will not violate an applicable NSPS or increment or any air quality standard.

Due to the nature of some subcategories of the non-fertilizer phosphate industry such as phosphorus production and defluorination of phosphate rock which handle large quantities of material and which require large quantities of fuel for thermal processes, there may well be a need for full PSD review of a new source facility. This may not be the case, however, if a smaller facility or less polluting facility is proposed. A small source of the designated pollutants (less than 50 tons/yr, 1,000 lb/day, or 100 lb/hr after abatement) is required only to apply for and obtain a preconstruction permit unless it would impact a Class I area. This may exempt many new source plants from full PSD review.

Nonattainment Areas

Even more stringent air quality regulations may be applied to new source facilities or significantly modified existing facilities in areas where ambient air quality standards are being exceeded (nonattainment areas). Permits will be required for construction and operation of major new or modified sources and applicants will be required to achieve the "lowest achievable emission rate" (LAER) of any pollutant which exceeds the standards. This rate is defined as a rate of emissions which reflects:

- the most stringent emission limitation in the applicable state implementation plan unless the applicant can demonstrate that such limitations are not achievable; or
- the most stringent limitation which is actually achieved in practice by similar facilities.

The Clean Air Act Amendments further require that the permit to construct and operate such facilities may be issued only if:

- by the time the facility is to commence operation, total allowable emissions from all existing and new sources in the Air Quality Control Region, including the new or modified facility, will permit reasonable further progress toward attainment of the applicable national ambient air standard for the identified pollutant; or
- the emissions of such pollutant from the new or modified facility will not cause the total emissions of the pollutant to exceed the allowance permitted by the implementation plan for the pollutant from all new or modified sources in the area.

The purpose of these requirements is to allow, under strict stipulations, the economic benefits to a region from introduction of new industry or new expansion of existing industry (new sources) to be obtained. The qualifying condition is that the new action must be accomplished in such a way as to assure progress toward compliance in the nonattainment area. Thus, permits issued by USEPA or the approved state agency must require "offsets" in the existing levels for pollutants which exceed Federal ambient air quality standards.

Emission Offsets

Offsets are enforceable reductions from the existing sources of air pollutants which will be greater than the emissions of those pollutants anticipated from the new source. A "new air quality benefit" must result from the combined new project plus the offsets attained (44 FR 3284, Part IV.A.4 and 44 FR 3275). In addition, the quantity of offsets must match the new source emissions on a "more than one-for-one" basis. The manner in which offsets may be attained is not specified. Several possible approaches which have been used include the following:

- when the new source is an expansion of an existing facility, the owner may install tighter controls on existing operations to achieve emissions which may be lower than those otherwise required for the existing sources;
- when the new source is an entirely new plant under a new owner in the nonattainment area, the applicant may reach an agreement with one or more existing sources whereby they agree to apply stricter pollution control measures, presumably in exchange for compensation by the new source applicant;
- in some instances, the applicant may purchase outright an existing facility, especially an obsolete facility with high pollutant emissions, and either clean it up or simply close it down;
- in cases where the state and/or local government are extremely interested in locating the new source industry in the area (for example, due to the benefits to the local economy), they may assist the applicant by either putting pressure on the existing sources to achieve stricter pollution control standards or by public works actions such as paving of roads in the area to help reduce background particulate emissions.

The amount of time required to process PSD applications could run to several years in some controversial cases and adequate lead time for design, for modeling of air quality effects, and for required monitoring (one year) should be anticipated. USEPA is committed to a policy of expediting permit application processing, public participation activities, and internal reviews so that the entire PSD review process could theoretically be carried out within 90 days after receipt of a complete and technically substantiated application. This time, however, could be extended by state review procedures, litigation, or offset arrangements in a highly industrialized nonattainment area. Hoffnagle and Dunlap (1978) emphasize that an industry

should allow adequate time for the one-year baseline monitoring. Review and approval by regulatory agencies of the design of the monitoring plan at the earliest possible time can be a time saver. Total time involved in the PSD process for the permit applicant may realistically range from 18-34 months, as illustrated below (Hoffnagle and Dunlap 1978):

Activity	Time for Activity (Months)	Cumulative Time (Months)
Specify monitoring required	1-2	1-2
Select vendors and contractors	0-3	1-5
Procure and install equipment	1-4	2-9
Conduct 1-yr baseline monitoring	12	14-21
Complete data analysis, modeling, and permit application	1-4	15-25
Request special model (if necessary) with agency hearing and review	0-6	15-31
Hearings on application and agency review	3-12	18-43

1.5.3 Solid Waste Regulations

The Resource Conservation and Recovery Act (RCRA), P.L. 94-580, defines "solid waste" as including solid, liquid, semisolid, or contained gaseous materials. Regulations implementing Subtitle C of the Act (40 CFR Part 261) provide that a solid waste is a hazardous waste if it is, or contains, a hazardous waste listed in Subpart D of Part 261 or the waste exhibits any of the characteristics defined in Subpart C. These characteristics include:

- Ignitability (flash point below 60° C (140° F)
- Corrosivity
- Reactivity
- Toxicity

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Hazardous wastes are identified in 40 CFR 261 Subpart D. The hazardous substances identified at this time in Subpart D do not include the major solid wastes of the non-fertilizer phosphate industry. However, additions are scheduled to be made to the list in the near future which will include solid wastes of the non-fertilizer phosphate industry as well. The only solid waste of the non-fertilizer phosphate industry that is definitely identified in these proposed regulations is "slag and fluid bed prills from processing phosphate ore to produce elemental phosphorus." This does not eliminate the possiblity of many other industry wastes having "hazardous" designations. Wastes containing arsenic or cadmium, for example, may be considered hazardous if the toxic materials can be leached out at concentrations of 5 mg/l and 1 mg/l respectively using the EP (Extraction Procedure) toxicity test. The nature of the wastes to be generated by a particular new source non-fertilizer phosphate plant will have to be carefully examined to determine the applicability of the hazardous waste designation.

All new facilities that will generate, transport, treat, store, or dispose of hazardous wastes must notify USEPA of this occurrence and obtain a USEPA identification number. Storage, treating, and disposal also require a permit.

The determination of whether wastes generated or handled are hazardous is the responsibility of the owner or operator of the generating or handling facility. The first step is to consult the promulgated list (40 CFR 261 Subpart D). Furnace slag from the production of elemental phosphorus, for example, is listed as a hazardous waste. If the waste is not listed, the second step is to determine whether the waste exhibits any of the hazardous characteristics listed through analytical tests using procedures promulgated in the regulations or by applying known information about the characteristics of the waste based on process or materials used.

If it is determined that a hazardous waste is generated, it should be quantified to determine applicability of the small generator exemption. This cutoff point is 2,200 pounds per month, but it drops to 2.2 pounds for any commercial product or manufacturing chemical intermediate having a generic name listed in Section 261.33. Containers that have been used to contain less

than 21 quarts of Section 261.33 materials and less than 22 pounds of liners from such containers are also exempt. It is anticipated that this exemption may be available to many very small plants with, for example, only one machine tool and one small painting operation. However, as more information is obtained on the behavior of substances in a disposal environment, the terms of this exemption may be altered from time to time.

The hazardous waste management system is based on the use of a manifest prepared by the generator describing and quantifying the waste and designating a disposal, treatment, or storage facility permitted to receive the type waste described to which the waste is to be delivered. One alternate site may be designated. Copies of the manifest are turned over to the transporter and a copy must be signed and returned to the generator each time the waste changes hands. If the generator does not receive a copy from the designated receiving facility or alternate within 35 days, he must track the fate of the waste through the transporter and designated facility or facilities. If the manifest copy is not received in 45 days, the generator must file an Exception Report with USEPA or the cognizant state agency.

A copy of each manifest must be kept for three years or until a signed copy is received from the designated receiving facility. In turn, the signed copy must be kept for three years. The same retention period applies to each Annual Report required whether disposal, storage, or treatment occurs on-site or off-site.

The generator must also:

- package the waste in accordance with the applicable DOT regulations under 49 CFR Parts 173, 178, and 179;
- label each package in accordance with DOT regulations under 49 CFR 172;
- mark each package in accordance with the applicable DOT regulations under 49 CFR 172;
- mark each container of 110 gallons or less with the following DOT (49 CFR 172) notice:

  "Hazardous Waste - Federal Law Prohibits Improper Disposal. If found, contact the nearest police or public safety authority or the U.S. Environmental Protection Agency."

- supply appropriate placards for the transporting vehicle in accordance with DOT regulations under 49 CFR Part 172, Subpart F.

Waste in properly labelled and dated containers in compliance with the regulations may be stored on the generator's premises for up to 90 days without a storage permit. This is to permit time for accumulation for more economic pickup or to find an available permitted disposal facility.

Due to the cost and stringent design and operating requirements for permitted landfills, it is anticipated that most new generator plants will utilize off-site disposal facilities. However, any companies desiring to construct their own will be subject to 40 CFR Part 264.

Incineration is considered to be "treatment," and, as such, is also subject to Part 264 as are chemical, physical, and biological treatment of hazardous wastes, and a permit will be required. Totally enclosed treatment systems--such as in-pipe treatment of acid and alkaline solutions--are not subject to this part.

Although underground injection of wastes constitutes "disposal" as defined by RCRA, this activity will be regulated by the underground injection control (UIC) program adopted pursuant to the Safe Drinking Water Act (P.L. 93-523). The consolidated permit regulations (40 CFR Parts 122, 123, 124) govern the procedural aspects of this program; the technical considerations are contained in 40 CFR 146.

The disposal of innocuous solid wastes is subject to Subtitle D of RCRA and the implementing regulations (40 CFR Part 256). Recovery or disposal in an approved sanitary landfill will be required under a state program. Disposal in open dumps is prohibited. All existing state regulations which do not meet the requirements of Subtitle D are superseded.

1.5.4 Other Government Regulations

There are various regulations other than pollution control that may apply to the siting and operation of facilities. Some of these regulations require that permits be obtained while others require only that the resource area in question be examined during the review process for issuance of pollution control and other permits. It is advisable to contact the appropriate agency to determine the applicability of a regulation to the project in question. Some Federal regulations that may be pertinent to a proposed facility include, but are not limited to, the following:

- Coastal Zone Management Act of 1972 (16 USC 1451 et seq.)
- Fish and Wildlife Coordination Act of 1974 (16 USC 661-666)
- National Environmental Policy Act of 1969 (42 USC 4321 et seq.)
- USDA Agriculture Conservation Service Watershed Memorandum 108 (1971)
- Wild and Scenic Rivers Act of 1969 (16 USC 1274 et seq.)
- Flood Control Act of 1944
- Federal-Aid Highway Act, as amended (1970)
- Wilderness Act of 1964
- Endangered Species Preservation Act, as amended (1973) (16 USC 1531 et seq.)
- National Historical Preservation Act of 1966 (16 USC 470 et seq.)
- Executive Order 11593 (Protection and Enhancement of Cultural Environment, 16 USC 470) (Sup. 13 May 1971)
- Archaeological and Historic Preservation Act of 1974 (16 USC 469 et seq.)
- Procedures of the Council on Historic Preservation (1973) (39 FR 3367)
- Occupational Safety and Health Act of 1970
- Executive Order 11988 (Floodplain Management - replaced Executive Order 11296 on 10 August 1966)
- Executive Order 11990 (Wetlands)

- Energy Policy and Conservation Act of 1975
- Energy Conservation and Production Act of 1976

Particular emphasis should be placed on obtaining the services of a qualified archaeologist to determine the potential for disturbance of an archaeological site, such as an early Indian settlement or a prehistoric site. Both the applicant and the archaeologist should stay in contact with the State Historic Preservation Officer (SHPO) throughout the entire process of siting the new facility. The National Register of Historic Places also should be consulted for historic sites such as battlefields.

The appropriate wildlife agency (state and Federal) should be contacted to ascertain that the natural habitat of a threatened or endangered species will not be affected adversely; other resource agencies also should be consulted to avoid or minimize impacts to areas that previously have been determined to be sensitive or uniquely important (wetlands, floodplains, prime farmlands, etc.).

From a health and safety standpoint, most industrial operations involve a variety of potential hazards and to the extent that these hazards could affect the health of plant employees, they may be characterized as potential environmental impacts. Company policy should provide and maintain safe and healthful conditions for employees and establish operating practices that will result in safe working conditions and efficient operations. All proposed plans to maximize health and safety should be described in the EID.

The plant must be designed and operated in compliance with the standards of the U.S. Department of Labor, the Occupational Safety and Health Administration, and the appropriate state statutes relative to industrial safety. Close coordination with local and/or regional planning and zoning commissions is recommended to determine possible building or land use restrictions. State and local regulations may exist that affect the facility, and the EID should indicate that these have been considered.

Table 15 presents a range of typical permits, licenses, certifications, and approvals that could be required from local, regional, state, and Federal officials for construction and operation of a major new source facility. Although this list doubtless will vary between jurisdictions, it is intended primarily to be illustrative. The new source NPDES permit review process normally will be expedited by documenting in the EID all known permits, licenses, and approvals that are needed to construct and operate the proposed plant, and the status of each.

Table 15. Typical permits, licenses, certifications, and approvals required from Federal, state, regional, and local authorities for construction and operation of a typical new source facility.

Agency	Requirement
• Local Planning Organization (regional, county, city)	• Rezoning of plant site
	• Approval of access road rights-of-way
• Local Department of Public Works	• Permit for filling or construction operations in floodplains
• Local Beautification Board	• Construction on public property if required
• Local Department of Development and Licensing	• Building permit for each structural component of facility
	• Use and occupancy permits
• State Planning Department	• Coastal zone construction permit, if required
• State Fire Marshal	• Permit to store flammable liquids
	• Approval of facility for fire protection
• State Department of Environmental Protection	• Water use and discharge permits
	• Test well permit
	• Commercial well permit
	• Permit for dewatering excavation
	• Permit for fuel oil storage tanks
	• Permit for solid waste disposal
	• Dredging, filling, or construction of intake structures
	• Sedimentation control approval

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Table 15. Typical permits, licenses, certifications, and approvals (continued).

Agency	Requirement
	• Noise control approval
	• State water quality certification
	• Construction permit for combustion equipment
	• Permit for handling, treatment, storage, or disposal of hazardous wastes
	• Registration of gaseous emissions
• State Air Pollution Control Department	• Permit for construction of stationary source of air pollutants
	• Permit for operation of stationary new source
	• Open burning of construction refuse
	• Review of indirect (mobile) emission sources
• State Board of Health	• Permit to construct and operate approved sewage disposal and potable water facilities
	• Permit for consumptive use of water, if applicable
• State Department of Highways and Transportation	• Permit for highway entrance of plant access road
	• Approval of public road improvements
	• Permits for oversize or overweight vehicles
• US Environmental Protection Agency (Regional Office)	• National Pollutant Discharge Elimination System (NPDES) permit for wastewater discharge
	• Prevention of Significant Deterioration of air quality (PSD) certification prior to commencement of construction activities

Table 15. Typical permits, licenses, certifications, and approvals (continued).

Agency	Requirement
	• Spill Prevention, Control, and Countermeasure (SPCC) plan
	• Hazardous/toxic waste disposal plan
• US Army Corps of Engineers, (District Office)	• Permit to construct structures or works* in navigable waters (Section 10, Rivers and Harbors Act of 1899)
	• Permit to dispose of dredged or fill materials in waters of the US (including wetlands) (Section 404)
(COE, Washington Office)	• Permit to construct any dam or dike in a navigable water of the US (Section 9, Rivers and Harbors Act of 1899)
	• Permit to ocean dump dredged materials (Section 103, Ocean Dumping Act)
	• Permit to discharge refuse matter into navigable waters of the US or their tributaries (Section 13, The Refuse Act of 1899)
	• Test boring on Federal land
• Occupational Safety and Health Administration	• Certification of safety and health criteria for plan operation (noise in the work place, etc.)

* Structures may include piers, breakwaters, bulkheads, revements, and aids to navigation; works may include dredging, stream channelization, excavation, and filling.

2.0 IMPACT IDENTIFICATION

This chapter presents an overview of the pollutants and impacts that could be expected due to the construction and operation of a new source non-fertilizer phosphate manufacturing facility and describes critical information and analyses that should be included in an EID. Pollutant generation and impacts have been quantified where possible to enhance the readers appreciation of the magnitude of any impacts. In addition to quantifying air emissions, wastewater discharges and solid wastes that may be generated by a new source, this chapter presents a discussion of the fate of industry pollutants in the environment. Impacts of the industry on energy and aesthetic resources as well as noise and socioeconomic factors are also discussed.

Part 2.1 of this chapter provides identification of the major pollutants associated with the industry and gives information on their sources and rates of discharge where such information is available. Part 2.2 identifies factors that should be included in an assessment of potential impacts as well as a generic discussion of pollutant toxicity.

2.1 PROCESS WASTES

The EID should present a complete description of the source, quantity, nature, treatment, and disposal of process wastes generated by the new source non-fertilizer phosphate facility. Because these materials may contribute to some of the most significant environmental impacts of the industry, a clear presentation of their origin and fate is of critical importance to the overall assessment of the consequences of operating a new source facility. Following are major waste streams and typical associated pollutant generation factors for the various subcategories of the non-fertilizer phosphate industry.

2.1.1 Air Emissions

Mass emission factors and air quality impact data for the non-fertilizer phosphate industry are sketchy. A Source Assessment of the industry has not been prepared by USEPA as of the publication of this document, and representative emission data are presently available only for portions of the industry.

In addition, the character of well studied emissions can vary significantly depending on the mineral content of the phosphate rock being used for phosphorus production or phosphate rock defluorination. Variations of this nature must be taken into account when quantifying projected raw emissions from the new source phosphate facility. The sources of emissions for the industry have been summarized in the following sections according to the process subcategories described in Chapter 1.0. Emission data have been included where available.

2.1.1.1 Phosphorus Production (Subcategory A)

The production of elemental phosphorus is a potentially significant air pollution generator. Significant emissions are generated by all three of the major operations: 1) furnace charge preparation, 2) electric arc furnace reduction, and 3) phosphorus recovery and storage (Stinson 1976). The pollutants generated during each of these operations are indicated in Figure 20.

Furnace Charge Preparation

Potential emission sources associated with furnace charge preparation include:

- raw material preparation and handling
- drying
- calcining
- transportation and weighing
- crushing and sizing
- storage

Pollutant emissions due to raw material handling and preparation are magnified by the bulk of materials required to produce elemental phosphorus. This is illustrated by the following generalized materials balance for the phosphorus production process (Stinson 1976):

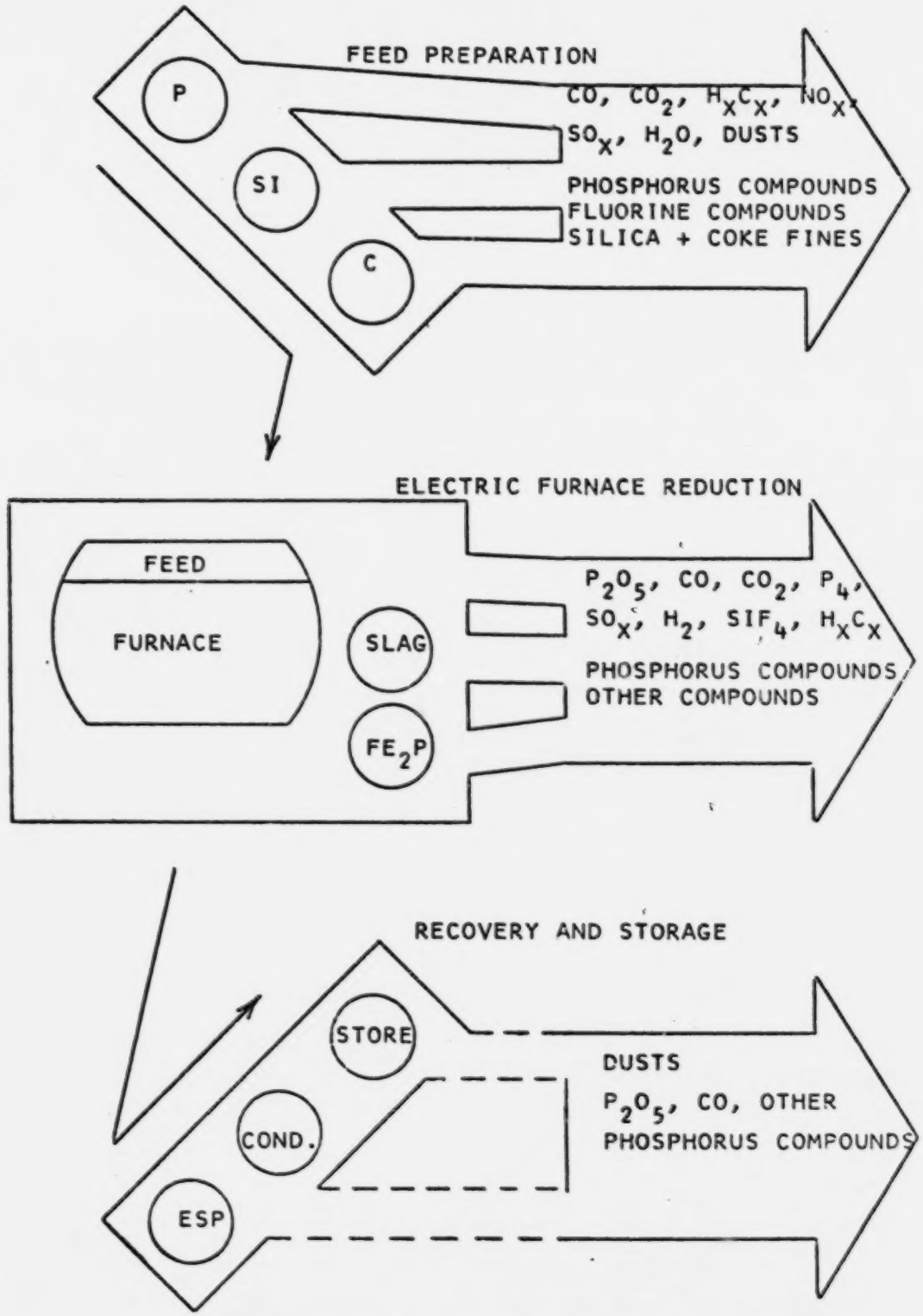

Figure 20. Raw emission types produced from phosphorus manufacture.

Source: Stinson, Mary, and F. Ellerbusch. 1976. Air pollution emissions and control from the manufacture of elemental phosphorus. USEPA, Industrial Env. Research Lab., Office of Research and Development, Edison NJ, 32 p.

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Input	Output
9.5 kkg phosphate rock	1 kkg phosphorus
1.1 kkg coke	8.9 kkg slag
1.7 kkg silica	0.3 kkg ferrophosphorous
0.4 kkg coal	2.8 kkg carbon monoxide
0.1-0.2 kkg iron	

Nearly 13 tons of raw material are required to produce one ton of elemental phosphorus.

The drying and calcining operations liberate carbon dioxide, fluorides, and particulates and are a more significant source than fugitive dust from raw material piles. The quantity of these emissions, particularly for fluorine, depends on the particular quality of rock and the furnace charge preparation process being used. Of the fluorine present in phosphate rock, approximately 20% to 50% is released through nodulizing and 30% to 40% is released by sintering (Stinson 1976).

Quantification of emissions from furnace charge preparation depends on the quality of phosphate rock being processed. Phosphate ores with a high ratio of fluoride to P_2O_5 will evolve fluorine at a lower furnace temperature than ores with lower ratios (Barber 1980b). Examples of typical phosphate rock mineral analyses are shown in Table 2 of Section 1.2.2, "Auxiliary Processes."

In addition to phosphate rock preparation, particulate emissions are generated by the handling of coke and silica, and the crushing, sizing, and storage of calcined furnace charge. Although the calcining kiln is heated with carbon monoxide off-gas from the electric furnace, it does not provide enough heat to run the agglomeration process. A supplemental fuel such as oil or coal must be used also. Sulfur dioxide emissions from the operation of the calcining kiln may be significant if not controlled.

Electrothermal Reduction

Potential emission sources associated with the electric arc furnace include (Stinson 1976; Barber 1980b):

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- Particulates from conveying system and proportioning bins;
- CO from the furnace feed bins;
- Fumes and particulates from slag and ferrophosphorus tapping operations;
- Fumes from venting CO fumes;
- Fumes from slag and ferrophosphorus cooling operations; and
- Fumes and particulates from miscellaneous openings in the furnace roof and gas offtake, rodout holes, electrode seals, and cracks in the furnace.

Furnace feeding operations from the bins atop the furnace may evolve large quantities of particulates. There is no seal between the bins and the furnace so pressure fluctuations within the furnace may allow emission of carbon monoxide (CO) and phosphorus (P_4) or draw air into the furnace with the CO and P_4 creating a potentially explosive situation.

When slag and ferrophosphorus are tapped from the furnace and cooled, fumes consisting of phosphorus oxides, fluorides, particulates, and SO_2 along with small quantities of trace metals such as vanadium are emitted. The rate of emissions from the tapping operation varies with their duration and frequency. Fluoride, SO_2, and P_2O_5 fumes evolved during the slag cooling operation depend on the method of quenching. Air quenching tends to evolve less fluorine than does water quenching (Stinson 1976). Ferrophosphorus is always air quenched, since it is highly reactive in the presence of water. Most fumes are controlled by the product recovery process and emission controls but emissions may still be a problem due to small, uncontrolled sources.

Phosphorus Recovery

Potential emission sources from the recovery of phosphorus include:

- Handling phosphorus-laden dust from the electrostatic precipitator.

- Contaminated carbon monoxide furnace fumes passed through the condenser.
- Fumes from phosphorus storage tank cleaning.

Approximately 125 kg dust/kkg P_4 is collected in the electrostatic precipitator and may contain as much as 1% phosphorus (Stinson 1976). Phosphorus pentoxide (P_2O_5) fumes may be evolved during the handling of precipitator dust or repair of the precipitator itself. Condensed furnace off-gas may contain phosphorus, silicon tetrafluoride, methane, and sulfur compounds in addition to carbon monoxide. The carbon monoxide wastestream is used as a fuel for calcining or localized heating, or may be flared. Condensed phosphorus is kept under a water blanket and produces no emissions. However, P_2O_5 may be evolved when phosphorus residuals come into contact with the air during cleaning of the phosphorus storage tanks.

2.1.1.2 Phosphorus Consuming (Subcategory B)

Emission problems of the phosphorus consuming processes vary widely. However, most emissions are captured by wet scrubbing devices and are transferred to the wastewater stream. Because 80% of the elemental phosphorus produced in the United States is used to manufacture "dry process" phosphoric acid, emissions from this source potentially may be the most significant overall (USEPA 1977d).

Phosphoric Acid

Potential emission sources associated with phosphoric acid production include (USEPA 1974):

- Tail gas emissions containing acid mists.
- Phosphorus fumes from leaks in the combustion chamber or transportation systems.

Tail gas emissions may contain submicron particles of phosphoric acid. There is also potential for phosphorus or toxic phosphoric emissions from fugitive sources.

Phosphorus Pentoxide

Potential emission sources from the manufacture of phosphorus pentoxide may include (USEPA 1973a):

- Phosphorus fumes from leaks in the combustion chamber.
- P_2O_5 fumes from the condenser barn or transportation of product.

Phosphorus Pentasulfide

Potential emission sources from the manufacture of phosphorus pentasulfide may include (USEPA 1973a):

- Casting fumes from production of solid P_2S_5.
- Dust from crushing of solid P_2S_5.
- Vented reaction gases from the batch reactor.

Phosphorus Trichloride

Potential emission sources from the manufacture of phosphorus trichloride include (USEPA 1973a):

- Hydrochloric and phosphorus acid fumes from condenser scrubber.
- Acid fumes from PCl_3 transfer and storage.
- Fugitive emissions from reactor cleaning.

Phosphorus Oxychloride

Potential emissions sources from the manufacture of phosphorus oxychloride include (USEPA 1973a):

- Hydrochloric and phosphoric acid fumes from condenser scrubber.

- Acid fumes from $POCl_3$ transfer and storage.
- Process vapors from the air oxidation variation of the $POCl_3$ process.

2.1.1.3 Phosphate Chemicals (Subcategory C)

Gaseous emissions are less of a problem for industrial phosphate productions than for other subcategories. However, phosphate particulate emissions are potentially significant due to product drying and handling procedures.

Sodium Tripolyphosphate

Potential emission sources from the manufacture of sodium tripolyphosphate may include (USEPA 1973a):

- Sodium phosphate mists from evaporator.
- CO_2 from the neutralization reaction.
- Dust and product fines from the spray drier and calciner.

Calcium Phosphates

Potential emission sources from the manufacture of calcium phosphates may include (USEPA 1973a):

- Fines from the monocalcium phosphate spray drying tower.
- Fines from kiln drying of dicalcium phosphate.
- Fines from the drum drying of tricalcium phosphate.

2.1.1.4 Defluorinated Phosphate Rock (Subcategory D)

The processes associated with the defluorination of phosphate rock are potentially significant emission generators. Large quantities of phosphate rock and sodium compounds must be handled and the calcining operation produces silicon fluoride and particulates (USEPA 1976a). Potential emission sources from this process may include:

- Dust from phosphate rock, silica or sodium carbonate handling, mixing, and drying.
- Sulfur compounds from heating the kiln or fluid bed reactor.
- Fluorine compounds such as hydrofluoric acid from calcining off-gas.
- Dust from product handling consisting of tricalcium phosphate and calcium silicates.

2.1.1.5 Defluorinated Phosphoric Acid (Subcategory E)

Information on the controlled emission of air pollutants from acid defluorination facilities has not yet been compiled by USEPA. However, the primary commercial method for defluorination of phosphoric acid is vacuum evaporation which essentially is identical to the procedure and equipment used for production of superphosphoric acid by the fertilizer industry. Information on controlled emissions from superphosphoric acid plants is available from the source assessment on the fertilizer industry (USEPA 1977d). Emissions from superphosphoric acid plants may serve as an indication of the levels that could be expected from a defluorination facility but these levels may not necessarily be applicable. Emission factors for these plants are presented in Table 16.

Typical data on the other two defluorination processes have not been compiled. The aeration process is quite new and may become more favored in the future, but the submerged combustion process has extensive emission scrubbing requirements and is not expected to enjoy expanded use in the future (USEPA 1977d).

2.1.1.6 Sodium Phosphates (Subcategory F)

Exact information is unavailable on emissions from the production of sodium phosphates from "wet process" phosphoric acid due to the proprietary nature of the process. Based on general descriptions of the process, emissions may be expected from the following operations:

- Handling of dry raw materials.

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Table 16. Average stack heights and controlled emission factors for "wet process" phosphoric acid and superphosphoric acid plants.

Emission Point	Stack Height, m	Emission Factor, g/kg P_2O_5		
		Total Fluorine	Particulate	SO_x
"Wet process" phosphoric acid:				
Rock unloading	12	0	0.15 ± 250%	0
Rock transfer and conveying	21	0	0.045 ± 180%	0
Wet scrubber system:	29			
Overall		0.010 ± 47%	0.054 ± 164%	0.032 ± 200%
With recovery of fluorine		0.0059 ± 61%	a	a
Without recovery of fluorine		0.012 ± 60%	a	a
Gypsum pond		0.025 to 2.5 avg 0.50	0	0
Superphosphoric acid:				
Wet scrubber	21	0.0073 ± 71%[b]	0.011 to 0.055	0

[a] Insufficient data to determine the effect of fluorine recovery on other emissions

[b] Accuracy based on standard deviation instead of "Student t" confidence limits due to only two data points.

Source: US Environmental Protection Agency. 1977d. Source assessment: Phosphate fertilizer industry - phosphoric acid and superphosphoric acid. Office of Research and Development, Washington DC. Prepared by Monsanto Research Corporation, Dayton OH, 93 p.

- Operation of calciners and dryers.
- Sulfur compound emissions from burning fuel for dryer heating.

2.1.2 Wastewater Characteristics

Wastewater generated by the various elements of the non-fertilizer phosphate industry generally contains high concentrations of phosphorus, fluorine, and dissolved solids, and is highly acidic. To a large degree, these pollutants are generated from the capture by various air pollution control devices such as wet scrubbers on the various emission sources. Other major sources of wastewater contamination include aqueous process solutions, slag quenching, condenser water, cooling water, and runoff.

Waste loads from the non-fertilizer phosphate industry have been characterized in two reports prepared by USEPA in connection with development of effluent limitations guidelines and standards (USEPA 1973a, 1976a). Data were collected from a number of plants representing a cross section of the manufacturers in each subcategory. Due to the age of the data and the increasing emphasis on control of all waste materials, it is possible that a new source facility would implement process changes and select equipment that would reduce their raw waste load to levels even less than those indicated. In view of this and the variability of pollutant generation for the various manufacturing processes, the nature of the wastewater for any new source phosphate plant should be documented by the applicant and specifically related to the particular processes and raw materials proposed.

2.1.2.1 Phosphorus Production (Subcategory A)

Wastewater is generated during phosphorus manufacture from the following sources (USEPA 1973a):

- Calciner and phosphorus furnace fume scrubbers.
- Phosphorus condenser (phossy water).
- Noncontact cooling water.

- Phosphorus sludge.
- Slag quenching.
- Phosphorus storage and transportation water (phossy water).
- Calciner heat source scrubber.

Scrubber Liquor

Air pollution control equipment may be the largest single source of contaminated wastewater from a phosphorus plant. Scrubbers are used to control emissions from the calciner, dust from phosphate rock, coke and silica feed and storage bins, condenser tailgas, and furnace taphole. These waste streams contain suspended solids, phosphates, sulfates, and fluorides. Fluorides are evolved as hydrogen fluoride or silicon tetrafluoride during calcining and thermal reduction of the phosphate rock and are hydrolized to hydrofluoride or fluosilicic acid in the scrubbers. Oxides of sulfur and phosphorus evolved during thermal treatment of phosphate rock produce sulfuric and phosphoric acid when hydrolized in the scrubber water. Suspended solids are also found in the form of Fe_2O_3 and SiO_2.

Phossy Water

Phossy water is produced both by the phosphorus recovery process condenser and by the need to store and transport the highly reactive phosphorus under a water blanket. Recycling of the phossy water is carried out to the maximum degree possible but mineral contamination makes it difficult to achieve total recycle. The problem with continuous recycle of phossy water can be explained as follows (Barber 1980b):

> In the phosphorus condensing system, furnace gases are contacted with water as part of the adiabatic cooling for condensation of phosphorus. Some water is lost by vaporization into the dry gas stream. However, water is used over and over in the condenser.
>
> In the phosphorus furnace about 9 percent of the fluorine in the phosphate is violatilized and comes over in the gases; 91 percent is combined in the slag. Some of the alkali metals--sodium and potassium--are volatilized from the funace. As a result, sodium fluosilicate and potassium fluosilicate salts accumulate in the re-

circulated condenser water. Since these salts have low solubility in water, saturation is reached by continuously recirculating the water and the fluosilicates will precipitate as scales in pumps, exhaust blower, spray nozzles, and piping causing stoppages and plant shutdowns. Consequently, some of the recirculating water must be bled off and replaced with fresh water to control the concentration of the scale-forming salts.

The phosphorus condensers may be constructed of mild steel or stainless steel. In the case of mild steel construction, the condenser water must be neutralized to prevent corrosion. When the water is neutralized with soda ash the scale-forming tendency is increased because the concentration of sodium fluosilicate is increased. Neutralization with ammonia is generally preferred because ammonium fluosilicate is more soluble than the sodium and potassium salts. With stainless steel construction, neutralization of the water is not required. The solubility of the fluosilicates is increased greater in acid solution than it is in neutralized solution. Nevertheless, if the recirculating condenser water were recycled indefinitely it would accumulate suspended solids and the viscosity would increase to the point that it would become difficult to pump, the spray nozzles would clog, and the system would loose its effectiveness for cooling the furnace gas.

The condenser water can be clarified and recycled to the condensing system. The elemental phosphorus content of the water is reduced from 1,770 ppm to 120 ppm by clarification. However, fluosilicates will accumulate and form scales unless some of the clarified water is replaced with fresh water. When condenser water is neutralized with ammonia to a pH of 5.5 to 6.0, about 1,300 gallons of water must be bled off per ton of phosphorus produced. The bleedoff rate is greater when soda ash is the neutralizing agent and less with acid condenser water. The elemental phosphorus content of the clarified water still exceeds the concentration that can be safely discharged by several orders of magnitude.

Phosphorus Mud or Sludge

A colloidal mixture of dust and phosphorus is collected in the condenser sump. The phosphorus sludge from the sump is stored in tanks to allow the high quality phosphorus to settle out. The resulting sludge may be centrifuged or filtered to remove more of the phosphorus. The sludge may be distilled to remove even more of the phosphorus.

Slag Quenching

Although it is almost always evaporated and not discharged, slag quenching water is of special concern due to the presence of uranium and its degradation products in phosphate rock. These, along with most of the fluorine and a

small quantity of the phosphate in the original rock, are concentrated in the slag. Fluoride and sulfate concentrations averaging 170 and 1,000 mg/l respectively may be found in the quenching water (USEPA 1973a). Concentrations of radioactive substances in quenching water are not likely to be high; however, the possibility exists that some radioactive substances may be picked up during slag quenching.

Cooling Water

Non-contact cooling water constitutes the largest water use in the phosphorus production process. It remains relatively uncontaminated, however, unless leaks or breaks develop in the system.

Typical raw wastewater characteristics for phosphorus producing facilities are presented in Table 17.

2.1.2.2 Phosphorus Consuming (Subcategory B)

No process wastewater is generated by the various manufacturing processes in the phosphorus consuming subcategory. However, contaminated water may result from other plant operations as indicated below:

- Phosphorus transportation and storage.
- Wet scrubbing of tail gases.
- Equipment cleaning.
- Leaks and spills.

Water contaminated with elemental phosphorus (phossy water) may be encountered in the waste stream of a phosphorus consuming operation due to spills or emergency conditions requiring a reactor dump. Due to its density and extreme reactivity (autoignition at 93° C), phosphorus settles into low spots in the sewer system and is dangerous to remove.

Hydrolysis of tail gases from the manufacture of phosphoric acid, phosphorus pentasulfide, phosphorus trichloride, and phosphorus oxychloride introduces phosphoric, sulfuric, and hydrochloric acid into the waste streams. Equipment cleaning may pick up reaction residues containing acid, phosphorus,

Table 17. Water use and process waste generation for major operations in the phosphorus production subcategory.

	Calciner Scrubber Liquor	Phosphorus Condenser Plus Other Phossy Water	Slag Quenching Water	Composite Waste
Waste water Quantity,				
l/kkg	300,000	100,000	25,000	425,000
gal/ton	72,000	24,000	6,000	102,000
Raw Waste Load, kg/kkg				
TSS	8.5	13.5	20.5	42.5
P_4	-	9	-	9
PO_4	2	22	1	25
SO_4	36	-	75	111
F	22	27	4.5	53.5
Total Acidity	60	-	-	54.5
Total Alkalinity	-	-	5.5	-
Raw Waste Load, lb/ton				
TSS	17	27	41	85
P_4	-	18	-	18
PO_4	4	44	2	50
SO_4	72	-	150	222
F	44	54	9	107
Total Acidity	120	-	-	109
Total Alkalinity	-	-	11	-
Concentrations, mg/l				
TSS	28	135	820	100
P_4	-	90	-	21
PO_4	7	220	40	59
SO_4	120	-	3,000	260
F	73	270	180	126
Total Acidity	200	-	-	128
Total Alkalinity	-	-	220	-

Note: Wastewater quantities and constituent concentrations are highly variable, depending upon degree of recirculation, but the raw waste loads should be representative.

Source: US Environmental Protection Agency. 1973a. Development document for proposed effluent limitations guidelines and new source performance standards for the phosphorus-derived chemicals segment of the phosphate manufacturing point source category. Office of Air and Water Programs, Washington DC, 159 p.

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carbon, iron, sulfur, chlorine, and arsenic compounds. However, most of these residues are removed as a solid waste rather than in the aqueous waste stream. Typical raw wastewater characteristics for phosphorus consuming operations are presented in Table 18.

2.1.2.3 Phosphate Chemicals (Subcategory C)

Contaminated wastewater is generated by the following sources during manufacture of phosphate chemicals (USEPA 1973a):

- Wet scrubbing of product fines.
- Filtrate from dewatering of food grade calcium phosphates.
- Leaks, spills, and equipment cleaning.
- Water softening.
- Defluorination of wet process phosphoric acid.

Finely divided particles of product from the drying operations are removed by wet scrubbing. Phosphoric acid mists also may be introduced into the wastewater stream from emission control systems. An excess of process water is used for the manufacture of dicalcium phosphate. The product slurry is dewatered by filtration or centrifugation prior to drying, which leaves a contaminated filtrate or centrate. Makeup water for the neutralization step requires softening, which produces a wastewater stream from regeneration of the softener. Leaks, spills, and equipment cleaning also may contribute raw material and product contaminants to the wastewater stream. When non-food grade calcium phosphates are produced, an additional wastestream is created from the defluorination of "wet process" phosphoric acid. This is discussed under Subcategory E. Typical raw wastewater characteristics from production of phosphate chemicals are presented in Table 19.

2.1.2.4 Defluorinated Phosphate Rock Subcategory (D)

Wastewater is generated during defluorination of phosphate rock from the following sources (USEPA 1976a):

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Table 18. Water use and process waste generation for production of major products of the phosphorus consuming subcategory.

Water or Waste Load	Product				
	Phosphoric Acid ("dry process")	Phosphorus Pentoxide	Phosphorus Pentasulfide	Phosphorus Trichloride	Phosphorus Oxychloride
	H_3PO_4 (75%)	P_2O_5	P_2S_5	PCl_3	$POCl_3$
Process Water Consumed					
l/kkg Pdt.	380	--	--	--	--
gal/ton Pdt.	92	--	--	--	--
Process Water Wasted: l/kkg Pdt	--	500	30,000	5,000	2,500
gal/ton Pdt.	--	120	7,200	1,200	600
Cooling Water Used: l/kkg Pdt.	91,000	29,000	16,600	54,000	50,000
gal/ton Pdt.	22,000	7,000	4,000	13,000	12,000
Phossy Water: P_4 conc, ppm	1,700	1,700	1,700	1,700	--
l/kkg P_4 consumed	580	580	580	580	--
kg/P_4/kkg P_4 consumed	1	1	1	1	--
gal/ton P_4 consumed	140	140	140	140	--
lb/ton P_4 consumed	2	2	2	2	--
Raw Waste Load, kg/kkg Pdt:					
HCl	--	--	--	3	2
H_2SO_3	--	--	1	--	--
H_3PO_3 + H_3PO_4	1	0.25	0.5	2.5	0.5
Raw Waste Load, lb/ton Pdt.					
HCl	--	--	--	6	4
H_2SO_3	--	--	2	--	--
H_3PO_3 + H_3PO_4	2	0.5	1	5	1
Concentrations, mg/l: HCl	--	--	--	600	800
H_2SO_3	--	--	34	--	--
H_3PO_3 + H_3PO_4	High	470	17	500	200

Source: U.S. Environmental Protection Agency. 1973a. Development document for proposed effluent limitations guidelines and new source performance standards for the phosphorus-derived chemicals segment of the phosphate manufacturing point source category. Office of Air and Water Programs, Washington DC, 159 p.

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Table 19. Water use and process waste generation for major products of the phosphate chemicals subcategory.

	Sodium Tripoly-Phosphate	Food Grade Calcium Phosphates		Animal Feed Calcium Phosphate	
		Dewatering	Particulate Scrubbing	Acid Defluorination	Particulate Scrubbing
Process Water Wasted:					
l/kkg Pdt.	0	2,100	2,100	6,300	420
gal/ton Pdt.	0	500	500	1,500	100
Raw Waste Load,					
TSS	-	50	50	-	225
Dissolved PO_4	-	15	15	-	4
HF, H_2SiF_6, H_2SiO_3	-	-	-	12	
Raw Waste Load, lb/ton Pdt:					
TSS	-	100	100	-	45
Dissolved P_4	-	30	30	-	8
HF, H_2SiF_6, H_2SiO_3	-	-	-	24	
Concentrations, mg/l:	-				
TSS	-	24,000	24,000	-	54,000
Dissolved PO_4	-	7,000	7,000	-	7,000
HF, H_2SiF_6, H_2SiO_3	-	-	-	1,900	-
TDS, mg/l	-	7,000	7,000	1,900	7,000

Source: U.S. Environmental Protection Agency. 1973a. Development document for proposed effluent limitations guidelines and new source performance standards for the phosphorus-derived chemicals segment of the phosphate manufacturing point source category. Office of Air and Water Programs, Washington DC, 159 p.

- Wet scrubbing of particulates and stack gases.
- Quenching water.
- Leaks and spills.

Particulates from handling of raw materials and hydrofluoric acid from hydrolysis of silicon fluoride in the tail gas are introduced to the wastewater stream by wet scrubbing. All process related water as well as cooling water and runoff, in many cases, is routed through a cooling/recirculation pond. Recirculated scrubber water is typically neutralized with lime before being returned to the plant from the recirculation pond. Solubilized tricalcium phosphate may also be picked up in the wastewater stream if water is used for quenching the defluorinated rock. Leaks, spills, and yard runoff also are sources of contaminated wastewater. Typical water use and raw wastewater characteristics from production of defluorinated phosphate rock are presented in Table 20.

2.1.2.5 Defluorinated Phosphoric Acid (Subcategory E)

Wastewater is generated during the defluorination of phosphoric acid from the following sources (USEPA 1976a):

- Wet scrubbing of stack and tail gases.
- Leaks, spills, and equipment cleaning.

Approximately 12 kg of fluosilicic (H_2SiF_6), hydrofluoric (HF), and silicic acid (H_2SiO_3) per kkg of defluorinated phosphoric acid are dissolved in the wastewater stream from emission control equipment (USEPA 1973a). Phosphoric and sulfuric acids may also be entrained by the emission control equipment during the defluorination process (USEPA 1976a). A small amount of wastewater is also generated by leaks, spills, and equipment maintenance. It should be kept in mind that all wastewater from this operation is recycled. Sample raw wastewater characteristics for this process are presented in Table 21.

Table 20. Water use and process waste generation for the defluorinated phosphate rock subcategory.

Total Process Water	45,894 l/kkg (11,000 gal/ton)
Makeup Water Required[1]	877 l/kkg (210 gal/ton)

Raw Waste Load	Concentration
pH	1.65
Total suspended solids (TSS)	16.00 mg/l
Total Solids	2,267.00 mg/l
Chloride (Cl)	101.00 mg/l
Sulfate (SO_4)	350.00 mg/l
Calcium (Ca)	40.00 mg/l
Magnesium (Mg)	12.00 mg/l
Aluminum (Al)	58.00 mg/l
Iron (Fe)	8.30 mg/l
Fluorine (F)	1,930.00 mg/l
Arsenic (As)	0.38 mg/l
Zinc (Zn)	5.20 mg/l
Phosphorus (P)	600.00 mg/l
BOD_5	3.00 mg/l
COD	48.00 mg/l
Color	#120 (after filter)
Turbidity	45.00 Jackson Candle Units

[1] Most defluorinated phosphate rock facilities operate on a complete recycle basis with a net consumption of water.

Source: U.S. Environmental Protection Agency. 1976a. Development document for effluent limitations guidelines and new source performance standards for the other non-fertilizer phosphate chemicals segment of the phosphate manufacturing point source category. Office of Water and Hazardous Materials, Washington DC, 105 p.

Table 21. Water use and process waste generation for the defluorinated phosphoric acid subcategory.

Total Process Water[1]	
Vacuum Evaporation Process	70,510 l/kkg (16,900 gal/ton)
Submerged Combustion	18,024 l/kkg (4,320 gal/ton)
Non-process water	43 l/kkg (14 gal/ton)

Raw Waste	Concentration
pH	1.29
Total suspended Solids	30.00 mg/l
Total solids	28,810.00 mg/l
Chloride (Cl)	65.00 mg/l
Sulfate (SO_4)	4,770.000 mg/l
Calcium (Ca)	1,700.00 mg/l
Magnesium (Mg)	106.00 mg/l
Aluminum (Al)	260.00 mg/l
Iron (Fe)	180.00 mg/l
Fluorine (F)	967.00 mg/l
Arsenic (As)	0.83 mg/l
Zinc (Zn)	5.30 mg/l
Total Phosphorus (P)	5,590.00 mg/l
BOD_5	15.00 mg/l
COD	306.00 mg/l
Color	#120 (after filter)[2]
Turbidity	45 Jackson Candle Units

[1] Most phosphoric acid defluorination facilities operate on a complete recycle basis.

[2] Unit of color - potassium chloroplatinate.

Source: U.S. Environmental Protection Agency. 1976a. Development document for effluent limitations guidelines and new source performance standards for the other non-fertilizer phosphate chemicals segment of the phosphate manufacturing point source category. Office of Water and Hazardous Materials, Washington DC, 105 p.

2.1.2.6 Sodium Phosphates (Subcategory F)

Contaminated wastewater is generated by the following sources during manufacture of sodium phosphates from "wet process" phosphoric acid:

- Calciner and phosphoric acid emission controls.
- Neutralization precipitation and filtration operations.
- Leaks, spills, and equipment cleaning.

If the "wet process" phosphoric acid used in the manufacture of sodium phosphates is produced on site, the phosphate rock is calcined to remove organic impurities. Emission control equipment or the calciner and acidulation equipment will introduce solids as well as acidic phosphorus, sulfur, and fluorine compounds into the wastewater stream. Sodium phosphate solutions are treated several times during the purification process to remove various impurities such as fluorine, arsenic, iron, aluminum, and silica present in the "wet process" acid. The precipitated impurities are removed at several steps in the process and the filtrates or centrates are discharged to the wastewater stream. A small amount of wastewater may also be generated by leaks, spills, and general equipment maintenance. Raw wastewater characteristics typical of sodium phosphate manufacture from "wet process" phosphoric acid are presented in Table 22. This wastewater must be treated before being discharged.

2.1.3 Solid Waste Characteristics

A variety of solid wastes are generated by non-fertilizer phosphate manufacturing operations. The most significant sources are slag from phosphorus production, process residues and by-products, precipitates from emission and water pollution control equipment, and general solid wastes from plant maintenance and bulk materials handling. Some of these solid waste materials may contain radioactive and toxic substances such as uranium, radium, and arsenic and are considered hazardous. Due to the potentially hazardous nature of many of the industry's raw materials and products, the composition of all waste material must be carefully documented in the EID and appropriate treatment and disposal measures must be identified.

Table 22. Water use and process waste generation for the sodium phosphates subcategory.

Total Water Supply	9,992 - 12,349 l/kkg (2,395 - 2,960 gal/ton)
Effluent Wastewater Discharge	7,600 - 10,000 l/kkg (1,830 - 2,400 gal/ton)

Raw Waste

Parameter	Concentration
pH	7.8
Total Suspended Solids	460 mg/l
Total Solids	2,100 mg/l
Chloride (Cl)	90 mg/l
Sulfate (SO_4)	240 mg/l
Calcium (Ca)	95 mg/l
Fluorine (F)	15.0 mg/l
Total Phosphorus (P)	250 mg/l
BOD_5	31.0 mg/l
COD	55.0 mg/l
Temperature	78°F

Source: U.S. Environmental Protection Agency. 1976a. Development document for effluent limitations guidelines and new source performance standards for the other non-fertilizer phosphate chemicals segment of the phosphate manufacturing point source category. Office of Water and Hazardous Materials, Wahington DC, 105 p.

Significant aspects of solid waste generation for each process subcategory are highlighted in the following sections.

2.1.3.1 Phosphorus Production (Subcategory A)

Large quantities of solid waste and by-product materials are produced during the manufacture of elemental phosphorus as indicated below (USEPA 1973a, Barber 1975):

Solid Waste or By-product/kkg Phosphorus Produced

Slag	8,900 kg/kkg	(17,800 lb/ton)	
Ferrophosphorus	300 kg/kkg	(600 lb/ton)	(By-product)
Dust	50-125 kg/kkg	(250 lb/ton)	(By-product)
Phosphorus sludge	25 kg/kkg	(50 lg/ton)	(By-product)

Slag is composed primarily of calcium silicate ($CaSiO_3$) with small quantities of other minerals as follows:

Typical Analysis of Phosphorus Furnace Slag (Barber 1975a)

Constituent	Percent (Dry Basis)	Concentration (ppm)
CaO	44.1	-
SiO_2	41.3	-
Al_2O_3	8.8	-
P_2O_5	1.3	-
F	2.8	-
K_2O	1.2	-
Na_2O	0.1-0.2	-
MgO	0.1-0.2	-
MnO	0.1-0.2	-
S	0.1-0.2	-
U*	-	30-200
Ra*	-	3-75
Th*	-	10

In the past, furnace slag has been sold as an aggregate or disposed of if no market could be found for it. Under the new RCRA regulations, however, slag will be classified as a hazardous waste due to the presence of significant quantities of radioactive materials and will require special handling and disposal (40 CFR 261.3). Ferrophosphorus is a valuable by-product consisting of several iron-phosphorus compounds: Fe_3, P, Fe_2P, FeP, and FeP_2. It is carefully handled and sold to users in the metallurgy industry. Dust collected by the electrostatic precipitators is made up of the following materials (USEPA 1977c).

P_2O_5 - 20-40%
K_2O - 12-16%
CaO - 6-16%
SiO_2 - 18-30%
C - 1-4%
F - 1-6%

A small quantity of sludge containing 10% dust, 30% water, and 60% phosphorus collects in the sump of the phosphorus condenser (USEPA 1973a). Sludge may be reprocessed to recover or utilize its phosphorus content while dust is oxidized to eliminate the residual phosphorus.

2.1.3.2 Phosphorus Consuming (Subcategory B)

Solid waste materials are generated as follows by the various processes producing chemicals from elemental phosphorus (USEPA 1973a):

Process or Product	Solid Waste/Unit Weight of Product
Phosphoric acid "dry process"	Arsenic sulfide 0.1 kg/kkg (0.2 lb/ton) Filter acid 0.75 kg/kkg (1.5 lb/ton)
P_2O_5	Waste silica from air drying unit
P_2S_5	Residue 0.60 kg/kkg (0.3 lb/ton) P_2S_5 dust 1 kg/kkg (2 lb/ton) Arsenic pentasulfide 0.05 kg/kkg (0.1 lb/ton)

PCl_3	Arsenic trichloride 0.05 kg/kkg (0.1 lb/ton)
	Still residue 0.05 kg/kkg (0.1 lb/ton)
$POCl_3$	Still residue 0.05 kg/kkg (0.1 lb/ton)

Arsenic is present in phosphate rock and is carried over with the phosphorus in the thermal reduction process. Small amounts of arsenic and product residues are generated during manufacture of anhydrous phosphorus derivatives. Although low in volume, these wastes are hazardous and require special handling.

2.1.3.3 Phosphate Chemicals (Subcategory C)

Very little solid waste is produced by manufacturing processes in this subcategory. Emissions of product fines from the drying operations generally are recovered from the scrubber stream and added back to the product line. Spilled material and floor sweepings are often used for making fertilizers. A notable exception to this is in the manufacture of food grade calcium phosphates where purity requirements prohibit the use of sweepings in the product. This amounts to approximately 10 kg of lime, grit, and calcium phosphate per kkg of product (20 lb/ton) (USEPA 1973a).

2.1.3.4 Defluorinated Phosphate Rock (Subcategory D)

A substantial quantity of solid waste is generated during the defluorination of phosphate rock. Most of the solids accumulate in a clarifier or the recycle pond due to settling and liming of the wet scrubber water (USEPA 1976a). Most of the precipitates occur in the form of calcium phosphates, calcium sulfate, and calcium fluoride which is toxic and must be afforded special handling. Other solid wastes from this subcategory include dust from bulk materials and general plant waste such as string, bags, and boxes.

2.1.3.5 Defluorinated Phosphoric Acid (Subcategory E)

Solid waste production for defluorinated phosphoric acid operations is similar to that for defluorinated phosphate rock. The largest source of solid

waste is the liming of the pond wastewater stream prior to discharge to produce calcium precipitates. If the defluorinated acid process is operated in conjunction with a "wet process" phosphoric acid plant as is typically the case, a common recirculation pond may be used to contain both the gypsum produced from the wet process acid and the calcium precipitates from the superphosphoric or defluorinated phosphoric acid operation.

2.1.3.6 Sodium Phosphates (Subcategory F)

A number of by-products and solid wastes are produced by the manufacture of sodium phosphates from "wet process" phosphoric acid as follows (USEPA 1976a):

- Fine solids may be captured during the rock calcining operation.
- Sodium fluosilicate is a by-product of the first neutralization step.
- Arsenic sulfate is precipitated from the acid.
- The second neutralization produces a voluminous sludge containing iron, aluminum, fluorine, and phosphorus pentoxide which is reclaimed as a fertilizer by-product.
- Fine solids may be captured during the handling of dry raw materials and products.

2.2 IMPACTS OF INDUSTRY WASTES

The non-fertilizer phosphate industry generates wastes that would cause severe, long-lasting impacts if introduced into the environment in the quantities and concentrations at which they are generated. The potential impacts of each recognized pollutant on impacted receiving media (i.e., air, water, land) should be identified in the EID based on its projected rate of generation and appropriate treatment. Because the industry generates wastes with relatively similar properties, the impacts of industry wastes will be discussed according to the pollutant characteristics rather than according to industry subcategories.

2.2.1 Air Impacts

Operations within this industry may generate emissions of the following pollutants:

- Fluorine compounds.
- Acid mists.
- Particulates.
- Phosphorus compounds.

Sulfur dioxide and particulates also may be generated from fossil-fueled calciner or dryer operations associated with several processes. The controls for the sources, however, can mitigate the impacts of these emissions on air quality and the environment. The potential impacts of these industry pollutants on human health and the environment are identified in Section 2.2.3.

Because New Source Performance Standards for the industry emissions have not been promulgated, industry impacts on air quality must be evaluated against ambient air quality standards. Based on industry emissions, a large new source facility may have to undergo the full PSD review and permit application procedure. This must be determined by USEPA and the state on a case by case basis, based on the estimates developed by the new source applicant in the EID.

The assessment of air quality impacts for a new source non-fertilizer phosphate facility may require the following measurements or studies for major sources such as phosphorus furnaces or phosphate rock defluorination facilities, but less stringent requirements may be applied to minor sources.

- Evaluation of emission rates from all potential contaminant sources (mobile and stationary) within the facility during its construction and operation.
- Discussion of the various available and proposed emission control techniques should describe contingency plans to be used if pollution control systems malfunction and the associated impacts.

- Where reliable representative data are not available, insurance of accurate measurements of facility performance and emissions, as well as ambient air quality and meteorology in the vicinity of the proposed new source facility before and during operation. Long-term air quality monitoring data may need to be obtained on the site to characterize existing conditions adequately.

- Atmospheric dispersion modeling to evaluate the short- and long-term effects of facility emissions and other neighboring emission sources on ambient air quality (cumulative and synergistic effects). A complete discussion of available air quality modeling techniques can be found in "Guideline on Air Quality Models," EPA-450/2-78-027 (USEPA 1978p) and in Section II.E. of a companion document to this one, "Environmental Impact Assessment Guidelines For New Source Fossil-Fueled Steam Electric Generating Stations" (USEPA 1979a).

- Potential for atmospheric chemical reactions that may result from plant emissions and produce new air contaminants.

- Discussion of projected ambient air contaminant levels with respect to Federal, state, and local ambient air standards and PSD increments.

2.2.2 Water Impacts

Many of the processes for the manufacture of phosphorus and non-fertilizer phosphate chemicals produce large quantities of highly contaminated aqueous wastes containing the following pollutants:

- Phosphorus and phosphate compounds.
- Fluorine compounds.
- Suspended solids.
- High acidity (low pH).

Effluent guidelines established for these parameters are discussed in Section 1.5.1.1. Significant concentrations of other pollutants including trace metals and toxic elements may also be present in industry wastewaters (USEPA 1973a, USEPA 1976a):

- Total dissolved solids.
- Temperature.

- Sulfates.
- Chlorides.
- Cadmium.
- COD.
- Vanadium.
- Arsenic.
- Uranium.
- Radium 226.

These pollutants require monitoring, but specific effluent guidelines have not been established. The new source applicant's EID should identify sources of the above and any other pollutants, expected discharge quantities, and effectiveness of proposed treatment technologies in controlling them. The applicant should clearly identify wastewater streams as well as process streams, because much of the industry's aqueous waste is reclaimed and reused within production processes and is not discharged to surface waters. The potential impacts of industry discharges on human health and the environment are identified in Section 2.2.3.

New source performance standards for the non-fertilizer phosphate industry generally require "no discharge" of process waste for all subcategories except production of sodium phosphates from "wet process" phosphoric acid. However, wastewater from such sources as non-point plant runoff and non-contact process equipment cooling may be discharged. In addition, provisions are made for infrequent discharges of process wastewater from the recycle/reuse ponds typically used by defluorinated phosphate rock and phosphoric acid facilities as described in Section 1.5.1.1.

The assessment of water resource impacts for a new source non-fertilizer phosphate facility will require an analysis to predict the potential effects of any industry discharges on surface and groundwater resources. Such an analysis will probably require the use of mathematical models to predict in-stream concentrations. Two of the most widely used and accepted models are:

- DOSAG (and its modifications).
- QUAL series of models developed by the Texas Water Development Board and modified by Water Resources Engineers, Inc.

These are steady-state, one-dimensional models useful in evaluating stream impacts. While these models are most often used to predict the decay of in-stream dissolved oxygen concentrations from discharges of organic wastes, they are also useful in predicting the fate of conservative type pollutants that are found in the phosphate industry's waste. The data required for these models include:

DOSAG-I

- Flow rates for system inputs and withdrawals.
- Information on reaches, junctions, stretches, headwater reaches.
- Reaction coefficients.
- Concentration of inflows.
- Stream temperature.

QUAL-II

- Identification and description of stream reaches.
- Initial conditions.
- Hydraulic coefficients for determining velocity and depth.
- Reaction coefficients.
- Headwater data.
- Waste loadings and runoff conditions.
- If temperature is to be modeled, also requires sky cover, wet bulb/dry bulb air temperature, atmospheric pressure, wind speed, evaporation coefficient, and basin elevation.

Other models are available for non-steady state conditions and two dimensions, as required for modeling estuaries, including:

- RECEIV and RECEIV II, developed by Raytheon for the USEPA Water Planning Division.

These models can evaluate both conservative (e.g., dissolved solids, metals) and non-conservative materials subject to first order reaction kinetics (e.g., BOD, DO). The data required as input to both of these models include:

- Tidal variations.
- Water surface elevations, area, and depth.
- Bottom roughness coefficients.
- Meteorological data, including rainfall, evaporation, and wind velocity and direction.
- Downstream boundary conditions.
- Junction and channel data.
- Water temperature.
- Initial pollutant concentrations.
- Inflow data.
- Oxygen saturation and reaeration coefficients.

In addition, there are many available water quality models that were developed in association with NPDES activities and the need for optimization of waste load schemes for an entire river basin.

2.2.3 Biological Impacts

The biological environment may be affected by certain pollutants from the various processes within the industry.

2.2.3.1 Human Health Impacts

The following listings summarize documented effects of primary and secondary pollutants on human health (USEPA 1974a).

Fluorides

Fluorides are rare in natural surface waters, but may occur in detrimental concentrations in groundwaters. Ingestion of fluoride compounds can result in:

- Lowering of tooth decay in children - 0.8 to 1.5 mg/l fluoride ion in drinking water.
- Mottling of tooth enamel in children, in quantities (varying with individuals) above 0.9 - 1.0 mg/l.
- Endemic cumulative fluorosis and skeletal effects in adults, in (varying) quantities above 3 or 4 mg/l.
- Death, or severe symptoms, in doses of 250-450 mg. Severe symptoms are "diffuse abdominal pain; diarrhea and vomiting; excessive salivation, thirst, and perspiration; and painful spasms of the limbs" (National Academy of Sciences 1971).

Experts disagree on how much airborne fluoride is dangerous, but believe that levels equivalent to workplace heavy exposure would be required. Apparently airborne fluorides are largely retained when ingested, but the dangers of airborne fluorides include resettling and transport into drinking water or vegetable food supplies (National Academy of Sciences 1971).

Total Suspended Solids (TSS)

Suspended solids include both organic and inorganic materials. Inorganic components include sand, silt, clay, fine raw materials and products such as phosphate rock particles, and certain insoluble products. The organic fraction includes such materials as grease, oil, tar, fats, various fibers, sawdust, and various materials from sewers. These solids may settle out rapidly and bottom deposits are often a mixture of both organic and inorganic solids. Besides the aesthetic displeasure associated with turbid waters or with bottom sludges when the suspended solids settle out, they can cause untreated water to be unpalatable and suspended particles can absorb pesticide and other chemical impurities that might not be transported otherwise in the water.

pH (Acidity/Alkalinity)

pH is a logarithmic expression of the concentration of hydrogen ions. At pH 7, hydrogen and hydroxyl (OH^-) ion concentrations in solution are essentially equal and the water is neutral. Lower pH values indicate acidity and higher values indicate alkalinity, in a nonlinear relationship. Extremes of pH are harmful or fatal to aquatic life, and dangerous to humans, but human contact with water of extremely high or low pH is usually avoidable:

- A deviation of 0.1 pH unit from 7.0 may result in eye irritation to swimmers; appreciable deviations cause severe pain.
- By effects on plumbing fixtures, water lines, and water works structures, pH below 6.0 can cause high levels of iron, zinc, copper, cadmium, and lead in drinking water.

Total Dissolved Solids (TDS)

In natural waters the dissolved solids consist mainly of carbonates, chlorides, sulfates, phosphates, and possibly nitrates of calcium, magnesium, sodium, and potassium, with traces of iron, manganese, and other substances. Although TDS levels above 500 mg/l in drinking water are progressively unpalatable, levels of:

- 4,000 mg/l are unfit for human use, except in hot climates where the salt content may be tolerable.
- 5,000 mg/l in drinking water causes bladder and intestinal irritation.

Cadmium

Cadmium in drinking water supplies is extremely hazardous to humans, and conventional treatment as practiced in the United States does not remove it. Cadmium is cumulative in the liver, kidneys, pancreas, and thyroid of humans and other animals. Human health effects include:

- A severe bone and kidney syndrome reported in Japan, from ingestion of as little as 600 mg/day.

- As a cumulative toxicant, cadmium causes insidious chronic poisoning in mammals and also fish and probably other animals.
- Organic compounds of cadmium may cause mutagenic or teratogenic (monstrous deformities) effects.

Phosphorus

Elemental phosphorus exists in three allotropic forms: white, red, and black (CRC 1967). The white form produced by the phosphate industry is highly reactive and is never found free in nature. It autoignites on contact with air and will cause severe burns if handled.

- Ingested, a fatal dose is 50 mg.
- The maximum recommended allowable concentration in air is 0.1 mg/m^3.

Arsenic

Arsenic is found to a small extent in nature in the elemental form. It occurs mostly as arsenites of metals or as mineral pyrites. If ingested, arsenic compounds can be a sudden or a cumulative poison:

100 mg - severe poisoning.

- 130 mg - possibly fatal poisoning.
- Smaller doses can accumulate and be fatal - arsenic accumulates in the body faster than it is excreted.

Uranium and Radium 226

Radioactive materials present a host of hazards through direct exposure or by accumulation in the biological ecosystem. The effects of these pollutants have been identified as follows (USEPA 1974a):

"Ionizing radiation, when absorbed in living tissue in quantities substantially above that of natural background levels, is recognized as injurious. It is necessary, therefore, to prevent excessive levels of radiation from reaching any living organism. Beyond the obvious fact that radioactive wastes emit ionizing radiation, they are also similar in

many respects to other chemical wastes. Man's senses cannot detect radiation unless it is present in massive amounts.

"Radium-226 is one of the most hazardous radioisotopes of the uranium decay scheme, when present in water. The human body preferentially utilizes radium in lieu of calcium when present in food or drink. Plants and animals concentrate radium, leading to a multiplier effect up the food web.

"Radium-226 decays by alpha emission into radon-222, a radioactive gas with a half life of 3.8 days. The decay products of radon-222, in turn, are particulates which can be absorbed onto respirable particles of dust. Radon and its decay products have short half lives and have been implicated in an increased incidence of lung cancer in those workers exposed to high levels (Bureau of Mines 1971). Heating or grinding of phosphate rock can liberate radon and its progeny to the surrounding atmosphere."

It may be added that ionized, airborne radon progeny attach readily to small dust particles that are easily lodged in the upper respiratory tract. Once there, their short half-lives lead to decay before they can be cleared from the lungs (Schiager 1978). The radioactive decay series for uranium and its decay products is presented in Table 23.

Guidelines for radiation exposure cannot be defined in terms of threshold values but it is agreed that exposure to radiation should be held to a minimum and should be encountered at all only when the necessity is justified.

2.2.3.2 Ecological and Environmental Impacts

The effects of pollutants generated by the industry may have the following impacts on the environment.

Phosphorus

Increases of phosphorus in surface waters have been linked to a wide range of direct and indirect ecological disruptions. These include:

- Proliferation of nuisance water plants.
- Accelerated eutrophication of water bodies.

Table 23. The radioactive decay series for uranium 238.

Nuclides	Half-Life	Specific Activity (Ci/G)	Decay Q(Mev) Beta	Energies Q(Mev) Alpha	Notes
U-238	4.51×10^{9} yr	3.3×10^{-7}		4.27	Parent
Th-Pa-U-234	2.47×10^{5} yr		2.48	4.86	
Th-230	8.00×10^{4} yr	1.9×10^{-2}		4.77	
Ra-226	1.60×10^{3} yr	0.99		4.87	Bone Seeker
Rn-222	3.82 day	1.5×10^{5}		5.59	Noble Gas
Po-218	3.05 min	2.8×10^{8}		6.11	Short-Lived
Pb-Bi-Po-214	46.5 min		4.32	7.84	Radon Progeny
Pb-Bi-Po-210	21 yr		1.22	5.41	
Pb-206					Stable
Series Totals:			8.02 +	43.7 =	51.72

Source: Schiager, Keith J. 1978. Radiation - a perspective. In Proceedings of an Environmental Symposium, The Fertilizer Institute, New Orleans LA, 6, 7, and 8 March 1978.

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- Bioaccumulation and toxicity (of elemental P) for marine fish.

The plant overgrowth and eutrophication aspect of the effects of increased phosphorus availability have specific negative effects:

- Dangerous to swimming, boating, and water skiing.
- Interferes physically with sport fishing.
- Interferes with development of fish populations.
- Vile stenches and tastes associated with water.
- Ineffectuates standard water treatment processes.
- Aesthetic effects.
  - reduced resort trade
  - lowered property values
- Contact rashes to human skin.
- Improved breeding environment for flies.

Fluorides

The effects of fluorides on the animal environment are related to vegetative accumulations and surface water contamination. Effects include:

- Chronic fluoride poisoning of livestock when water contains 10-15 mg/l.
- Shorter-term fluoride poisoning of livestock when water ration contains 30-50 mg/l.
- Toxicity to fish in concentrations above 1.5 mg/l.

The effects of acute poisoning in livestock include (National Academy of Sciences 1974):

- Restlessness.
- Stiffness.
- Anorexia.

- Reduced milk production.
- Nausea and vomiting.
- Incontinence of urine and feces.
- Necrosis of mucosa of digestive tract.
- Weakness and severe depression.
- Cardiac failure.

Chronic toxicosis is not always distinguishable from acute symptoms, but also results in (National Academy of Sciences 1974):

- Debilitating osteoarthritis and lameness.
- Dental enamel lesions.

Although milk production in livestock is affected, fluoride transfer to the milk is very slight. With poultry, however, a greater concentration of fluoride does show up in the eggs.

Suspended Solids

In the aquatic environment suspended solids cause a number of problems:

- Turbid waters decrease photosynthetic activity of aquatic plants.
- Settled solids on stream or lake beds
  - eliminate normal benthic species;
  - reduce dissolved oxygen available in the area;
  - stimulate populations of benthic sludgeworms and associated organisms.

pH Effects

Extremes of rapid fluctuations in pH level can create problems to aquatic organisms including:

- Rapid death and associated rotting of fishkills, and generation of algal blooms.

- Increased toxicity of other dissolved substances in the water, such as
  - matalocyanide
  - ammonia.

Dissolved Solids

Dissolved solids levels in water affect aquatic organisms and in general make water troublesome for industrial uses and for irrigation. Effects on the ecosystem include:

- Loss of habitat at 5,000 - 10,000 mg/l for species of freshwater fish.
- Death to freshwater fish when salinity is changed rapidly.
- Increased toxicity of heavy metals and organic compounds to fish and other aquatic life.

Temperature

Temperature is one of the most important and influential ecological water quality characteristics. Temperature determines those species that may be present; activates the hatching of young, regulates their activity, and stimulates or suppresses their growth and development; attracts, and may kill when the water becomes too hot or becomes chilled too suddenly. Colder water generally suppresses development. Warmer water generally accelerates activity and may be a primary cause of aquatic plant nuisances when other environmental factors are suitable.

Temperature is a prime regulator of natural processes within the water environment. It governs physiological functions in organisms and, acting directly or indirectly in combination with other water quality constituents, it affects aquatic life with each change. These effects include chemical reaction rates, enzymatic functions, molecular movements, and molecular exchanges between membranes within and between the physiological systems and the organs of an animal.

The specific mechanisms and results of elevated temperature extremes include:

- Higher chemical reaction rates.
- Decreased DO.
- Increased bacteria production.
- Spawning perturbations.
- Increases in predator, parasite, and competing species populations.
- Fish food alterations.
- Increased synergistic reactivity of pollutants.
- Increase in green and blue-green algae and decrease in number and distribution of benthic organisms (food chain disruption).
- In the presence of sludge, increased gas formation and multiplication of saprophytes and fungi.

Cadmium

Cadmium pollution problems are derived from direct toxicity and synergistic actions with other metals. These include:

- Acute and chronic poisoning of aquatic and terrestrial species.
- Synergistically increases toxicity of copper and zinc
- Concentration of cadmium in marine organisms, particularly molluscs.

Chromium

The toxicity of chromium salts toward aquatic life varies widely with the species, temperature, pH, valence of the chromium, and synergistic or antagonistic effects, especially that of hardness. Fish are relatively tolerant of chromium salts, but fish food organisms and other lower forms of aquatic life are extremely sensitive. Chromium also inhibits the growth of algae.

In some agricultural crops, chromium can cause reduced growth or death of the crop. Adverse effects of low concentrations of chromium on corn, tobacco, and sugar beets have been documented.

Zinc

Zinc exhibits toxic effects on both freshwater and saltwater aquatic organisms. The following effects have been observed:

- Concentrations of zinc in the range of 0.1 to 1.0 mg/l in soft water is lethal to fish.
- The presence of copper in the water increases the toxicity of zinc.
- The presence of calcium or hardness decreases the relative toxicity of zinc.
- Invertebrate marine organisms are very sensitive to zinc. As little as 30 ug/l retards growth of the sea urchin.
- Long-term sub-lethal effects have been observed in the marine environment.
- Zinc sulfate is lethal to many plants.

Vanadium

Vanadium and its compounds cause physiological disorders in mammals. The major concern, however, is for effects in the aquatic ecosystem. The following effects on aquatic species have been observed:

- The toxicity of vanadium varies inversely with the hardness of the water.
- The common bluegill fish can be killed by 6 ppm in soft water and by 55 ppm in hard water.
- Other fish are similarly affected.

Arsenic

Arsenic ions and compounds can be lethal and harmful in both water and soil environments. Typical effects are:

- An accumulative poison in oysters and shellfish.
- Arsenic trioxide is extremely harmful to some fish species (5.3 mg/l for 8 days).

- Arsenic trioxide is lethal to mussels at 16 mg/l in 3 to 16 days.
- Certain food crops are made unmarketable grown in water with 1 mg/l of arsenic
- Soils containing 4-12 mg/kg are unproductive.

Uranium and Radium 226

The life spans of many animal species are not long enough to show adverse effects of low level radiation, but radionuclides tend to be accumulated in the food chain so that the greatest danger is to species high on the food chain. The potential effects for human health, or for economic disaster, are severe when food species accumulate potentially dangerous levels of radionuclides (resulting in a ban on production if controls are enforced). The most significant pathway to humans is through the accumulative effects on fish and shellfish, or through drinking water.

All of the factors noted above can affect the quantity and quality of aquatic resources. Shifts in these resources caused by pollution will alter aquatic communities, but the magnitude and overall significance of such changes will vary according to their specific agent. For example, industrial phosphate wastes can stimulate growth of algae. However, such an increase in productivity (eutrophication) leads to an overall decrease in water quality and species diversity in the system as shown by many studies on lakes.

The effects of pollutional stress may be both immediate and delayed. Organisms may be killed outright by the altered conditions of their habitat. For example, fish kills can result when pH is reduced drastically or when respiration is impaired because gill membranes are clogged by sediment and suspended solids. A more subtle impact results from sub-lethal stress effects. Weakened organisms may be unable to function efficiently and may succumb to disease. The ability to avoid predators may be reduced, their reproduction rates may be decreased, and their usefulness as a food supply diminished due to concentration of toxic substances. Thus, both the acute and chronic effects of pollution act to destabilize natural communities.

2.3 OTHER INDUSTRY IMPACTS

The phosphate chemical industry can have significant impacts on public health and the ecology if pollutants from the industry processes are uncontrolled. The industry can have other impacts that are not directly generated by the chemical process. Wastes from the industry can also affect public utilities and other pollution control systems. These potential impacts must be addressed in the EID.

2.3.1 Aesthetics

If included as a part of an integrated phosphate complex, a new source non-fertilizer phosphate facility could be associated with large and complex operations occupying hundreds of acres. Rock storage and handling areas, haul roads, rock conveyors, recycle ponds, solid waste storage piles, dust, erosion, and sediment-laden streams can be aesthetically displeasing. Particularly in rural and suburban areas, phosphate chemical manufacturing (and possible associated mining activity) can represent a noticeable intrusion on the landscape. Measures to minimize the aesthetic impacts of the project must be developed during site selection, plant planning design, and construction. The applicant should consider the following factors where feasible to reduce potential aesthetic impacts:

- Existing Nature of the Area. The topography and major land uses in the area of the candidate sites are important. Topographic conditions and existing trees and vegetational visual barriers can be used to screen the operation from view. A lack of topographic relief and vegetation would require other means of minimizing impact, such as regrading or planting of vegetation buffers.

- Proximity of Parks and Other Areas Where People Congregate for Recreation and Other Activities. The location of public use areas should be mapped and presented in the EID. Representative views of the plant site from observation points should be described. The visual effects on these recreational areas should be described in the EID in order to develop the appropriate mitigation measures.

- Transportation System. The visual impact of new access roads, rail lines, haul roads, barge docking, pipelines, and storage facilities on the landscape or waterfront should be considered. Locations, construction methods and materials, and maintenance should be specified.

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2.3.2 Noise

The major sources of noise associated with phosphate chemical manufacturing include:

- Plant construction equipment (bulldozers, graders).
- Raw material transport systems (haul roads, conveyors, loading dozers).
- Rock grinding and handling.
- Boilers and steam venting.
- Product transport systems (truck, railroad, and barge loading).
- Air pollution control equipment.

These activities can create significant ambient noise levels that may decrease with increasing distance from the site. Noise can be attenuated partially with thick stands of vegetation or other barriers (Bolt Beranek & Newman 1973). Even at distances of 1,500 to 2,000 feet the increases in noise levels due to manufacturing activities still may be noticeable. Sensitive noise receptors within a half mile of a major manufacturing facility are of potential concern and should be documented in the EID.

Noise also can create serious health hazards for exposed workers; therefore, the necessary source and operational control methods should be employed. Such measures include:

- Enclosed process machinery.
- Mufflers on engines.
- Lined ducts.
- Partial barriers.
- Vibration insulation.
- Imposed speed limits on vehicles.
- Scheduled equipment operations and maintenance.

The USEPA has recommended a maximum 75 dBA, 8-hour exposure level to protect workers from loss of hearing. A maximum 55 dBA background exposure level is recommended to avoid annoyance during outdoor activity (USEPA 1974c). A suitable methodology to evaluate noise generated from a proposed new source facility would require the applicant to:

- Identify all noise-sensitive land uses and activities adjoining the proposed plant site (e.g., schools, parks, hospitals, and businesses in the urban environment; homes and wildlife sanctuaries in the rural environment).
- Measure the existing ambient noise levels of the areas adjoining the site.
- Identify existing noise sources in the general area, such as traffic, aircraft flyover, and other industry.
- Determine whether there are any state or local noise regulations that apply to the site.
- Calculate the noise level of the phosphate facility processes, and compare that value with the existing area noise levels and the applicable noise regulations.
- Assess the impact of the operations's noise and, if required, determine noise abatement measures to minimize the impact (e.g., quieter equipment, noise barriers, improved maintenance schedules).

2.3.3 Energy

Several of the products of the non-fertilizer phosphate industry, particularly elemental phosphorus, have high energy requirements as indicated in Table 24. Increasing costs are forcing the industry to ever larger facilities in order to achieve an acceptable economy of scale (USEPA 1973a). A new source phosphorus producer or defluorinated phosphate rock producer could tax local electric energy or natural gas supplies in some areas with their large energy requirements. Such potential impacts as well as potential energy conservation measures would be evaluated in any preliminary industrial planning report but potential conservation measures should be evaluated as well.

Table 24. Process energy requirements of phosphorus and phosphate chemical manufacturing operations.

Product	Energy Requirements	
	Electricity	Fuel
Phosphorus (P_4)	12,500 kwh/ton	12,000 ft^3 natural gas/ton
Phosphoric acid (H_3PO_4)	60 kwh/ton P_2O_5	--
Phosphorus pentoxide (P_2O_5)	85 kwh/ton	--
Phosphorus pentasulfide (P_2S_5)	7.8 kwh/ton	80 lbs steam/ton
Phosphorus trichloride (PCl_3)	24.5 kwh/ton	760 lbs steam/ton
Phosphorus oxychloride ($POCl_3$)	25 kwh/ton	730 lbs steam/ton
Dicalcium phosphate (feed grade)	18.2 kwh/ton	100,000 BTU/ton
Dicalcium phosphate dihydrate	37 kwh/ton	1,100,000 BTU/ton
Defluorinated phosphate rock	- -	5,000 ft^3 natural/gas/ton
Defluorinated phosphoric acid	70 kwh/ton	1,800 ft^3 natural gas/ton
Sodium phosphates (wet acid)	38.9 kwh/ton	13,900,000 BTU/ton

Sources: US Environmental Protection Agency. 1973b. Economic analysis of proposed effluent guidelines, industrial phosphate industry. Office of Planning and Evaluation, Washington DC.

US Environmental Protection Agency. 1974b. Economic analysis of proposed effluent guidelines, non-fertilizer phosphate manufacturing industry. Office of Planning and Evaluation, Washington DC.

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At a minimum, the applicant should provide the following information in the EID:

- Total external energy demand for operation of the facility.
- Total energy generated on site.
- Energy requirements by type.
- Sources of energy off-site and alternatives.
- Use of electric generating capacity during non-peak hours
- Proposed measures to conserve or reduce energy demand and to increase efficiency of operation.

2.3.3.1 Cogeneration

Cogeneration in industrial processes denotes any form of the simultaneous production of electrical or mechanical energy and useful thermal energy (usually in the form of hot liquids or gases) (USDOE 1978).

Opportunities for cogeneration should be identified at any new source operation. The Public Utility Regulatory Policies Act of 1979 provides for Federal Energy Regulatory Commission rules favoring cogeneration facilities, and requiring utilities to buy or sell power from qualified cogenerators at just and reasonable rates.

Extensive cogeneration is not practiced at most non-fertilizer phosphate facilities; however, some internally generated energy sources are used. The most notable example is the use of furnace off-gas from phosphorus production to provide a portion of the heat required for agglomeration of the furnace charge. Nonetheless, the EID should indicate the power demands of processes to be used and assess the potential for excess steam capacity for generation of marketable or internally useable electric power.

2.3.3.2 Energy Conservation

Although the non-fertilizer phosphate industry is not one of the major energy consumers on a national scale, energy conservation practices are of benefit to the producer, regional energy supplies, and the economy as a whole. The EID should identify opportunities for energy conservation at the new

source manufacturing facility and indicate the costs and benefits of their implementation. Examples of energy conservation measures that should be considered include:

- Use of low temperature furnace charge agglomeration methods for phosphorus producers. This may include pulverization and combination of furnace charge with clay binders followed by low-temperature calcination or formation of agglomerates using fertilizer industry techniques such as "wet process" phosphoric acid sludge for a binder (Barber 1980a).

- Particulate collection systems are designed to provide optimum dust pickup and transport velocities. Long and complicated ducts give rise to duct stoppages or expenditure of excessive energy to transport dust at high enough velocity to prevent stoppages (Barber 1978).

- Baghouse collectors are used instead of scrubbers for particulate collection when the particulates have low hygroscopicity and the gas temperature does not exceed the limit for fabric filters. Baghouse collectors consume less energy than scrubbers unless gases have to be heated to overcome the hygroscopicity problem. When the gases have to be heated, energy for baghouses and scrubbers is about the same (Barber 1978).

- Phossy water effluent may be reused in the process or the effluent may be sold as a fluid fertilizer. This saves energy for nutrient production and eliminates a waste treatment facility (Barber 1978).

In addition, well-planned siting of the plant can greatly affect net energy consumption of the operations. The amount of energy consumed in transportation by the four major transportation modes is shown below in Btu's/ton-mile (Achorn & Kimbrough 1974):

Pipeline	450
Barge	500
Rail	700
Truck	2,500-2,800

These data indicate that to conserve energy the applicant should use pipeline, barge, and perhaps rail as much as possible, and avoid truck transportation. One ton of elemental phosphorus contains phosphorus equivalent to 2.29 tons of P_2O_5 and 4.24 tons of merchant grade, wet process phosphoric acid. Thus it is generally more economical to transport phosphorus to a manufacturing point near its point of final use than it is to ship manufactured products or raw phosphate rock over long distances.

Finally, uranium production which can have significant effects on energy supply should be considered if the facility has an associated phosphate rock mine.

2.3.4 Socioeconomics

The introduction of a large new phosphate facility into a community may cause land use, economic, and social changes. Therefore, it is necessary for an applicant to understand the types of impacts of changes that may occur so that they can be evaluated adequately. The importance of these changes usually depends on the size of the existing community where the facility is located. The significance of the changes caused by a facility of a given size normally will be greater near a small rural community than near a large urban area. This generally is due to the fact that a small rural community is likely to have a nonmanufacturing economic base and a lower per capita income, fewer social groups, a more limited socioeconomic infrastructure, and fewer leisure pursuits than a large urban area. There are situations, however, in which the changes in a small community may not be significant, and, conversely, in which they may be considerable in an urban area. For example, a small community may have had a manufacturing (or natural resource) economic base that has declined. As a result, such a community may have a high incidence of unemployment in a skilled labor force and a surplus of housing. Conversely, a rapidly growing urban area may be severely strained to provide the labor force and services required for a new phosphate facility.

The rate at which changes occur (regardless of the circumstances) also is often an important determinant of the significance of the changes. The applicant should distinguish clearly between those changes occasioned by the construction of the facility, and those resulting from its operation. The former changes could be substantial but usually are temporary; the latter may or may not be substantial, but normally are more permanent in nature. The potential impacts which should be evaluated include:

- Increased consumption and rate of land development.
- Land use pattern and compatibility changes.
- Economic base multiplier effects.
- Population size and composition changes.
- Increased labor force participation and lower unemployment rates.
- Increased vehicular traffic and congestion.
- Loss of prime agricultural land and environmentally sensitive areas.
- Increased demand for community facilities and services.
- Increased demand for water supply, sewage treatment, and solid waste disposal facilities.

During the construction phase, the impact will be greater if the project requires large numbers of construction workers to be brought in from outside the community than if local unemployed workers are available. The potential impacts include:

- Creation of social tension.
- Short-term expansion of the local economy.
- Demand for increased police and fire protection, public utilities, medical facilities, recreation facilities, and other public services.
- Increased demand for housing on a short-term basis.
- Strained economic budget in the community where existing infrastructure becomes inadequate.
- Increased congestion from construction traffic.

Various methods of reducing the strain on the budget of the local community during the construction phase should be explored. For example, the company itself may build the housing and recreation facilities and provide the utility services and medical facilities for its imported construction force. Or the company may prepay taxes, and the community may agree to a corresponding reduction in the property taxes paid later. Alternatively, the community may float a bond issue, taking advantage of its tax-exempt status, and the company may agree to reimburse the community as payments of principal and interest become due.

During operation, the more extreme adverse changes of the construction phase are likely to disappear. Longer run changes may be profound, but less extreme because they evolve over a longer period of time and may be both beneficial and adverse.

The new source applicant should document fully in the EID the range of potential impacts that are expected and demonstrate how possible adverse changes will be handled. For example, an increased tax base generally is regarded as a positive impact. The revenue from it usually is adequate to support the additional infrastructure required as the operating employees and their families move into the community. The spending and respending of the earnings of these employees has a multiplier effect on the local economy, as do the interindustry linkages created by the new industry. Backward linkages are those of the facility's suppliers. Forward linkages are those of the facility's markets.

Socially, the community may benefit as the increased tax base permits the provision of more diverse and higher quality services, and the variety of its interests increases with growth in population. Conversely, the transformation of a small community into a larger community may be regarded as an adverse change by some of the residents who choose to live in the community as well as by those who grew up there and stayed because of its small town amenities.

The applicant also should consider the economic repercussions if, for example, the quality of the air and water declines as a result of various emissions from the phosphate facility. In some cases, other more traditional sectors of economic activity may decline because labor is drawn away from them into higher paying phosphate related or tertiary sector activities. As an illustration, the fishing sector may decline if water pollution increases, or if fishermen abandon the occupation in favor of employment at the phosphate facility. Again, the tourist sector may decline if air and water pollution is noticeable or if the landscape is degraded.

Thus, the applicant's framework for analyzing the socioeconomic impacts of the location of a phosphate facility must be comprehensive. Most of the changes described can and should be measured to assess fully the potential

costs and benefits. The applicant should distinguish clearly between the short-term (construction) and long-term (operation) changes, although some changes may be common to both (e.g., the provision of infrastructure). The significance of the changes depends not only on their absolute magnitude, but on the rate at which they occur. The applicant should also develop and maintain close coordination with State, regional, and local planning and zoning authorities to ensure full understanding of all existing and/or proposed land use plans and other related regulations.

USEPA's Office of is developing a methodology to be used to forecast the socioeconomic impacts of new source industries and the environmental residuals associated with those impacts.

2.3.5 Raw Materials and Product Handling

In most instances potential major problems related to shipping, storing, and handling of raw materials and products are well identified and systems are in place or methods available to keep these problems in check.

Continuing use of phosphate rock as the industry's basic resource is assured and any special problems should be discussed that cause impacts related to the mining area where the majority of the phosphate processing will be conducted. Phosphate mining in North Carolina is carried on adjacent to the Pamlico Estuary below the water table. Cofferdams and pumps are used to expose phosphate deposits 100 feet deep. Even though the facility is well managed, eutrophication in the estuary occurs as the result of phosphate laden pumping waters being discharged to waters with significant nitrogen levels. The wastes of phosphoric acid production also are disposed in this high water level environment. Potential for leaching and for sedimentation and contamination of surface waters is high, especially during hurricane conditions.

In Florida, the significant special problems are related to new mining areas. The richer deposits still unmined lie below deeper overburdens and some deposits are in several layers. Higher volumes of overburdens must be moved and replaced. The effects of this problem on phosphate processing are

less limiting and can be useful as supplies of sands and tailings for gypsum pond dewatering.

Effects of phosphate production on transportation facilities in new source industries should be assessed. Florida, North Carolina, and Gulf Coast facilities have good access to ocean, barge (river and intracoastal), pipeline, rail, and truck transportation. Similar advantages may not be enjoyed by the western mining area; however, the EID should identify advantages of alternate transportation modes. When properly controlled, pipeline and barge transportation offers both environmental and economic advantages.

Since most facilities are near mines, stockpiles of phosphate rock are not necessary. However, some phosphorus producers in the west stockpile huge quantities of phosphate rock for winter operation or for mixture with local ore to produce a better furnace charge. Facilities that purchase phosphate rock should specify storage arrangements to prevent particulate air emissions and rainfall runoff of waters contaminated with phosphorus and TSP. The EID should state whether the storage area will be exposed to the weather and what the impacts of fugitive particulate emissions and runoff waters would be.

Due to the fact that many of the non-fertilizer phosphate industry's products are corrosive, highly reactive, toxic, flammable, or combinations of these, their handling and transportation must be carefully controlled. Among the industry's product handling problems are:

- ferrophosphorus
- elemental phosphorus
- phossy water

The handling of phosphorus and associated phossy water is one of the industry's most pervasive problems. Phosphorus must always be stored under a water blanket which always contains suspended colloidal phosphorus that is very difficult to remove. In practice, phossy water is usually treated and reused by phosphorus producing plants while phosphorus consuming plants collect it from storage tanks or rail cars and send it back to the producing plant for treatment (USEPA 1977c). The EID should identify the proposed means for handling phossy water from any new source phosphorus producing or consuming facility.

By-product ferrophosphorus, like phosphorus, is highly reactive. However, unlike phosphorus it is stable in air but explodes violently upon contact with water. Safety precautions for handling ferrophosphorus should be identified in the EID.

2.3.6 Special Problems in Site Preparation and Facility Construction

The environmental effects of site preparation and construction of new phosphate manufacturing facilities are common to land disturbing activities on construction sites in general. Erosion, dust, noise, vehicular traffic and emissions, and some loss of wildlife habitats are to be expected and minimized through good construction practices wherever possible. At present, however, neither the quantities of the various pollutants resulting from site preparation and construction nor their effects on the integrity of aquatic and terrestrial ecosystems have been studied sufficiently to permit broad generalizations. Therefore, in addition to the impact assessment framework provided in the USEPA document, Environmental Impact Assessment Guidelines for Selected New Sources Industries, the permit applicant should tailor the conservation practices to the site under consideration in order to account for and to protect certain site-specific features that warrant special consideration (e.g., critical habitats, archaeological/historical sites, high quality streams, or other sensitive areas on the site). All mitigation/conservation measures that are proposed should be discussed in the EID.

Erosion Control During Construction.

The major pollutant at a construction site is loosened soil that finds its way into the adjacent water bodies and becomes "sediment." Common remedial measures include, but are not limited to, proper planning at all stages of development and application of modern control technology to minimize the production of huge loads of sediment. Specific control measures include:

- Use of paved channels or pipelines to prevent surface erosion.
- Staging or phasing of clearing, grubbing, and excavation activities to avoid high rainfall periods.

- Use of storage ponds to serve as sediment traps where the overflow may be carefully controlled.
- Use of mulch or seeding immediately following disturbance.

If the applicant chooses to establish temporary or permanent ground cover, grasses normally are more valuable than shrubs or trees because of their extensive root systems that entrap soil. Grasses may be planted by seeding, sodding, plugging, or sprigging. During early growth, grasses should be supplemented with mulches of wood chips, straw, and jute mats. Wood fiber mulch has also been used as an antierosion technique. The mulch, prepared commercially from waste wood products, is mixed into a slurry and sprayed on the land with a hydroseeder.

Site Selection Factors

The EID should include information to indicate the capacity of the soils and geology to accommodate production and waste storage. Problems which would require special consideration include:

- Unstable soils.
- Steep topography.
- Presence of wetlands.
- Location relative to floodplains.
- Permeability of soils.
- Erosion problems during construction and operation.

The applicant is responsible for assessing the effects of the proposed facility on groundwater quality and quantities. The areas of particular relevance to the phosphate manufacturing industry are:

- Potential and effects of seepage of gypsum pond wastewaters into aquifers.
- Potential for groundwater contamination from storage piles of raw materials and waste gypsum.

- Use of groundwater for process and make-up water.

In western states water supply can be a limiting factor. The EID should evaluate effects of water consumption in terms of both groundwater and surface water supplies in the region.

3.0 POLLUTION CONTROL TECHNOLOGY

The new source industry must install and operate pollution control systems that reduce the actual discharge of pollutants into the environment to levels defined by the New Source Performance Standards (NSPS). The technologies selected to attain these reduction levels are to be selected by the industry and are not mandated by USEPA. However, this chapter describes the technologies used by USEPA in defining the levels that are appropriate for NSPS. Where such technologies have not been identified by USEPA, state-of-the-art control techniques that could be evaluated by the applicant are discussed. The permit applicant must demonstrate in the EID that NSPS will be met.

3.1 STANDARDS OF PERFORMANCE TECHNOLOGY: AIR EMISSIONS

New Source Performance Standards (NSPS) for air emissions have not been identified specifically by USEPA for non-fertilizer phosphate facilities; therefore, the most recent applicable technology should be identified for control of industry emissions. In general, emission control technologies may be divided into groups consisting of in-process controls and end-of-process-controls. A new source industry may use both types of controls.

3.1.1 Controllable Emissions

Major sources and types of emissions from the non-fertilizer phosphate industry were identified in Section 2.1. The most significant pollutants from the industry are particulates generated from raw materials handling, thermal reactions, and the drying and handling of dry products; and fluorides removed from phosphate rock and products. Smaller amounts of sulfur dioxide, phosphorus pentoxide (P_2O_5), and acid mists also are emitted during manufacturing operations. Due to the similarity between the emission problems faced by most segments of the industry, air pollution abatement equipment tends to be similar. In general, wet scrubbing systems are used on most emission sources because of the presence of both particulates and hydrolyzable gas streams such as hydrogen fluoride, and sodium tetrafluoride. In the past electrostatic precipitators and baghouse filters have been successfully used where dry dust and particulates alone are the problem. However, electrostatic precipitators and bag-

houses have been greatly improved and are being examined as an alternative to high energy wet scrubbers for dry, fine particulate control.

3.1.2 In-Process Emission Control Technologies

Many pollutants, particularly dust from raw materials handling, may be eliminated or controlled at their source by containment. Large uncovered stockpiles of raw materials kept on site may cause minor dust problems, but the movement and processing of these materials represent more significant emission sources. Some gaseous emission problems also may be reduced at their source by modifications to the production process. Following are several examples of in-process controls that may be applicable to control of emissions from particular operations of the industry.

- Dust Control

  Enclosed operation and baghouses are typical methods of control at phosphate rock handling locations. Satisfactory control of dust emissions from unloading hopper-bottom railroad cars or trucks at phosphate fertilizer plants is achieved by the use of flexible skirts around bases of the vehicles to contain dust and flexible-contact hoods to channel emissions to baghouses.

  Feed hoppers, storage bins, and conveyors usually are enclosed to reduce particulate emissions and moisture contamination of phosphate rock in the fertilizer industry. Similar control techniques also may be applicable to raw materials handling for several categories of the non-fertilizer phosphate industry. When transport of ground rock from storage bin to feed hopper is accomplished by pneumatic conveyors, a cyclone separator and baghouse may be located at the destination to control bulk material and discharged dust (USEPA 1979a).

- Reduction of PCl_3 and $POCl_3$ Emissions

  Chlorides once dissolved in the wastewater stream are difficult to remove, but reduction of emissions before they reach the scrubbers can help eliminate this problem. PCl_3 and $POCl_3$ emissions from the reactor/still can be reduced by maintaining a low vapor pressure using refrigerated condensers and demisters downstream of the reactor. Refrigerated condensers on storage vessels also can help reduce emissions from that source by keeping the product in its liquid phase.

- Reduction of P_2S_5 Emissions

  The major emissions from production of P_2S_5 are the fumes from casting molten P_2S_5 in air. These can be eliminated by either casting in a vacuum or casting in an inert gas atmosphere.

- Collection of Open Emissions

  In the phosphorus production subcategory problems may be encountered in controlling open process emission sources such as slag and ferrophosphorus tapping. Dense clouds of corrosive, combustible gases containing fine particulates, fluorine, sulfur, and phosphorus are released during furnace tapping. Vacuum hood and duct systems are usually installed to collect these fumes for treatment by a scrubber system (Stinson 1976).

The most effective and probably most difficult in-process emission controls to implement are process changes. Certain process variations offer lower emissions or more easily controllable emissions as a significant side benefit. In-process controls or modifications should be considered by the applicant at every available opportunity to reduce emissions and reduce the cost of treating them.

3.1.3 End-of-Process Emission Controls

End-of-process emission controls reduce industry emissions and may have an important role in determining the wastewater and solid waste characteristics of the industry. Basic air pollution control equipment that may have application to the control of industry emissions includes dry collectors and scrubbers. Several types are described in this section.

3.1.3.1 Dry Collectors

Dry collection devices are used primarily for removal of particulates; however, they frequently are used as precleaning units for gas adsorption or scrubbing units to remove larger particles. The most commonly used devices are described below:

- Cyclone

  A cyclone is essentially a type of gravity settler employing centrifugal force rather than gravitation for solids separation. The spinning motion may be imparted to the carrier gas by tangential gas inlets, vanes, or a fan (USDHEW 1969). The operation of one type of cyclone is indicated in Figure 21. Most cyclones are capable of removing particles ranging in size down to 15 to 40 microns. A cyclone may be used ahead of a baghouse electrostatic precipitator or scrubber to reduce the solids loading to that equipment.

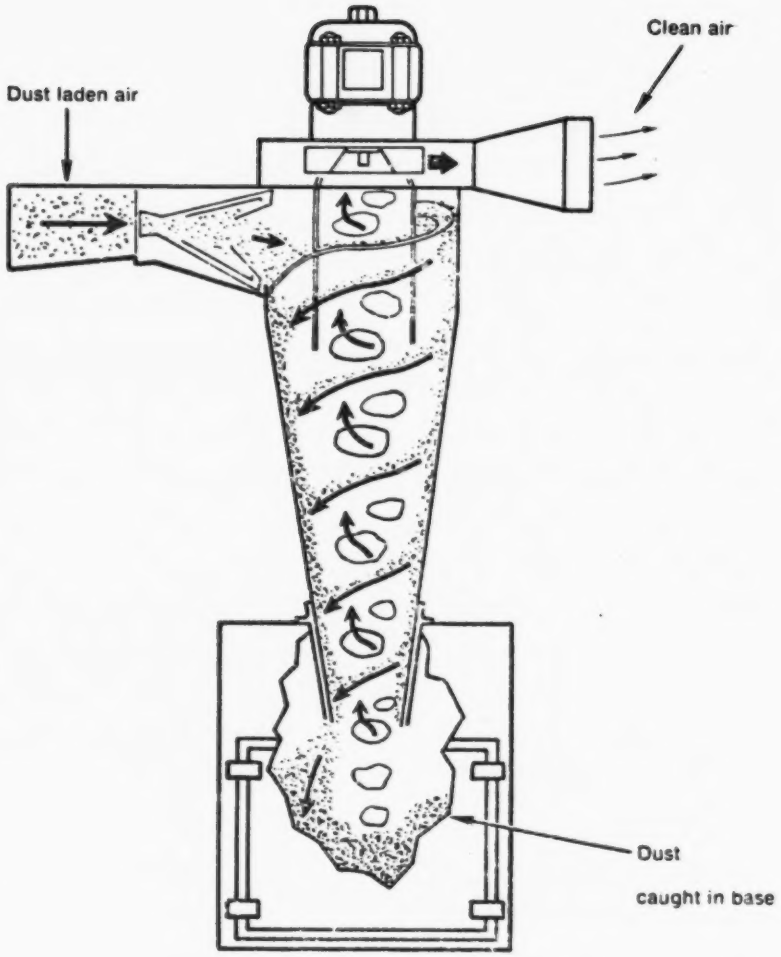

Figure 21. Cyclone scrubber.

Source: U.S. Environmental Protection Agency. 1978q. Environmental pollution control, textile processing industry. Prepared by the Torit Corporation.

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- Baghouses

  Baghouses are essentially structures containing fabric bags which remove particulates by direct filtration. A typical baghouse filter is illustrated in Figure 22. The initial filtration efficiency and pressure drop through a filter are low, but as a mat of dust collects on the filter both the pressure drop and the efficiency increase. Once established, the dust mat performs most of the filtration and efficiencies of 99+% are achieved. Cleaning is accomplished by mechanical vibration of the bag or reverse air flow. Baghouses are not suitable for collection of small sized carbonaceous material such as coke fines due to the potential fire hazards. More information is available in the USEPA Air Pollution Engineering Manual (Danielson 1973).

  Other filtration devices include fabric mist eliminators which remove such pollutants as acid mists from emission streams. Droplets condense on a fiber matrix and flow down to a collection point.

- Electrostatic Precipitators

  Electrostatic precipitators are useful for control of acid mists and small particle emissions; however, they are sensitive to variations in the character of the gas stream and may not be equally effective on all emissions. This device operates by first passing the emission stream through an ionizing grid where the dust is given a positive charge. These charged particles are then attracted to a negatively charged plate where they are collected. Electrostatic precipitators can be used for collection of dust down to the 0.1 micron range with 95-99% efficiency. These systems offer the advantage of low pressure drop and a low power requirement but are quite large and require a high initial investment. More information is available from the USEPA Air Pollution Engineering Manual (Danielson 1973).

3.1.3.2 Wet Scrubbers

Most of the air pollutants produced by the non-fertilizer phosphate industry are in combined streams consisting of both particulates and gases such as fluorine. The ability of wet scrubbing systems to remove both fine particulates and gaseous pollutants simultaneously has led to their predominance as an emission abatement technology in the industry. They can be used to control explosive gases without a fire hazard or reduce the temperature of hot gases by evaporation. They are also compact and have a well developed technology. Many scrubber designs also are able to utilize contaminated, recycled water from the recycle pond as a scrubbing medium without serious problems. This is important due to the no-discharge limitation placed on the industry by NSPS.

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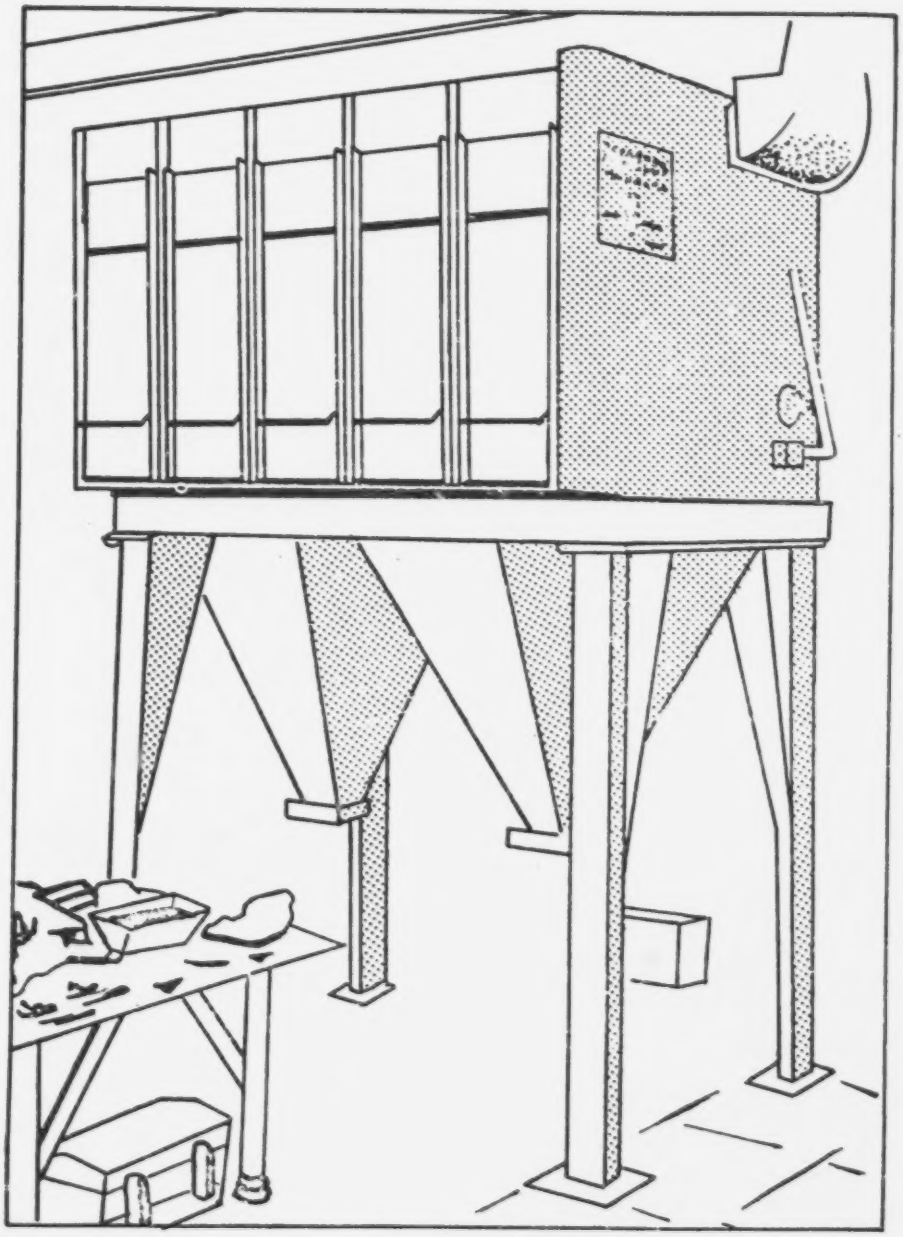

Figure 22. Typical baghouse unit.

Source: U.S. Environmental Protection Agency. 1978q. Environmental pollution control, textile processing industry. Prepared by the Torit Corporation.

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In general, the efficiency of a scrubber in removing particulate matter is related to the energy input. Particle collection efficiency of a scrubber is improved by increasing the relative velocity and decreasing the diameter of the collecting media. This explains the energy/efficiency relationship of scrubbers. Removal of a high percentage of particles requires removal of the finest materials, which necessitates a large energy input to increase the velocity and reduce the diameter of scrubber droplets. The relative energy input in terms of pressure drop versus minimum particle size removed for various types of scrubbers is indicated below:

	Pressure drop, inches of water	Minimum particle size (microns)
Spray towers	0.5-1.5	10
Cyclone spray scrubbers	2-10	2-10
Impingement scrubbers	2-50	1-5
Packed- and fluidized-bed scrubbers	2-50	1-10
Orifice scrubbers	5-100	1
Venturi scrubbers	5-100	0.8
Fibrous-bed scrubbers	5-110	0.5

Source: Perry, Robert H., and Cecil H. Chilton (Eds.). 1973. Chemical engineers handbook. 5th ed. McGraw Hill, New York NY.

Wet scrubbing systems also are used for removal of gaseous pollutants from the emission stream. For the non-fertilizer phosphate industry this typically involves hydrolyzing hydrogen fluoride, silicon tetrafluoride, sulfur dioxide, or some other gaseous oxide to an acid in the scrubber media. These are transferred to the new source wastewater streams and are significant contributors to the industry's water pollution problems. The direct reuse of scrubber water in treating emissions from phosphate rock calciners and defluorination systems is limited by process requirements, but treated water plus makeup may be relimed in the recirculation pond before being reused as a scrubber medium. Many of the most common scrubber technologies are described below. More information on scrubbers is available in the USEPA Scrubber Handbook, Volumes I and II (Calvert et al. 1972).

- Venturi Scrubbers

Venturi scrubbers are primarily high efficiency particulate collection devices but they also are applicable to gas adsorption problems and are in widespread use throughout the industry. They are particularly well suited to treating emission streams containing large amounts of solids or silicon tetrafluoride because of their high solids handling capability and self-cleaning characteristics. Operational reliability and low maintenance requirements are major reasons for the popularity of this scrubber design (USEPA 1977d).

A venturi scrubber provides a high degree of gas-liquid mixing, but the relatively short contact time and the concurrent flow of the scrubbing liquid tend to limit its absorption capabilities. A typical venturi scrubber unit is illustrated in Figure 23. When effluent streams requiring a high degree of fluoride removal are treated, venturis are often used as the initial component in a multiple-scrubber system.

- Cyclonic Spray

This scrubber atomizes the scrubbing liquid using the hydraulic pressure developed by the liquid pump. The higher the pump pressure the finer will be the spray droplet and the more effective the absorption of gaseous pollutants. This unit introduces the gases into a well defined spray zone and assures complete coverage of waste gases. The spray is removed from the gases by spinning. The cyclonic scrubber requires a 2-6" WG pressure drop and liquid pressures of 50-150 psig. They require between 4 and 8 gal/1,000 cfm. Because of the use of spray nozzles, these units require fairly high quality scrubbing liquid. The cyclonic scrubber has proven to be an excellent absorber of gaseous contaminants such as fluoride (Hill 1976). A typical cyclonic scrubber setup is illustrated in Figure 24.

- Impingement Scrubbers

These devices use a large number of small diameter orifices with impingement target devices located downstream from the orifice holes. Due to the use of small orifices and close tolerances, these units are subject to plugging if there are other contaminants or reactants within the scrubbing process. This limits their application in instances where recycle water is used as a scrubbing medium (Hill 1976).

- Packed Scrubbers

The packed scrubber brings the liquid and gas into contact within the zone of packed elements. The two basic principles employed in packed scrubbing are the counterflow of gases flowing upward through the packed bed section with the liquid being introduced above the packing and flowing downward through the packing. The crossflow washer has a horizontal gas flow through a packing with the water being introduced normal to the gas flow. Typical examples of this type of scrubber are illustrated in Figure 25. These units have proven to be the most

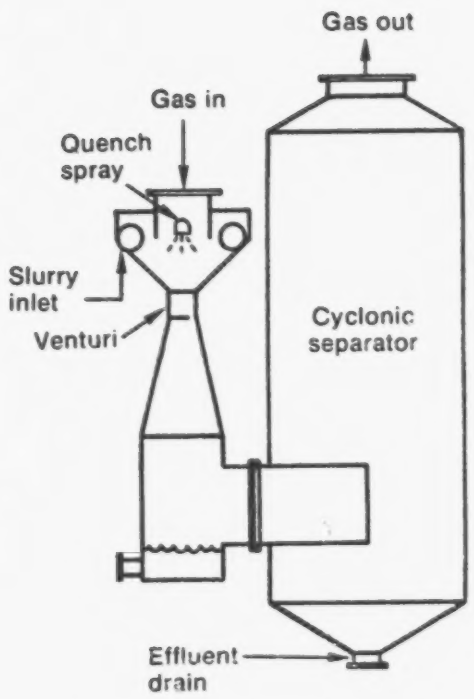

Figure 23. Typical venturi scrubber unit.

Source: US Environmental Protection Agency. 1978q. Environmental pollution control, texitle processing industry.

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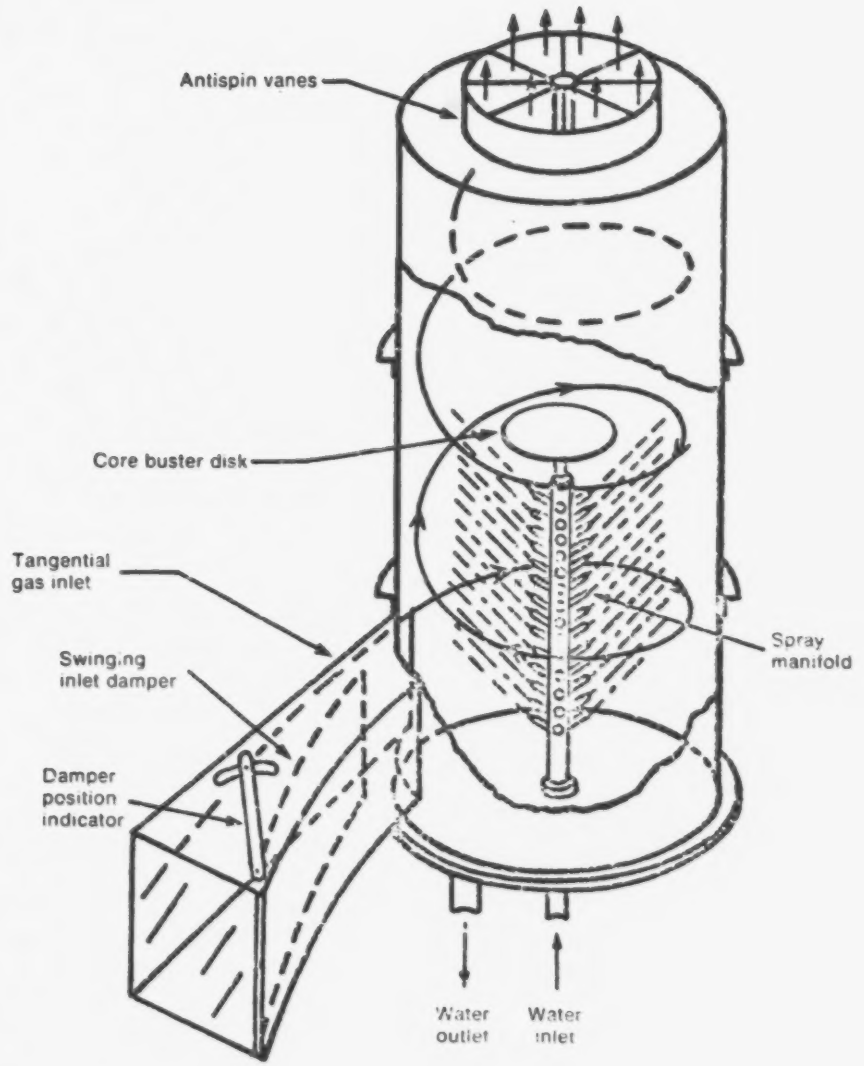

Figure 24. Typical cyclonic spray scrubber unit.

Source: US Environmental Protection Agency. 1978q. Environmental pollution control, textile processing industry.

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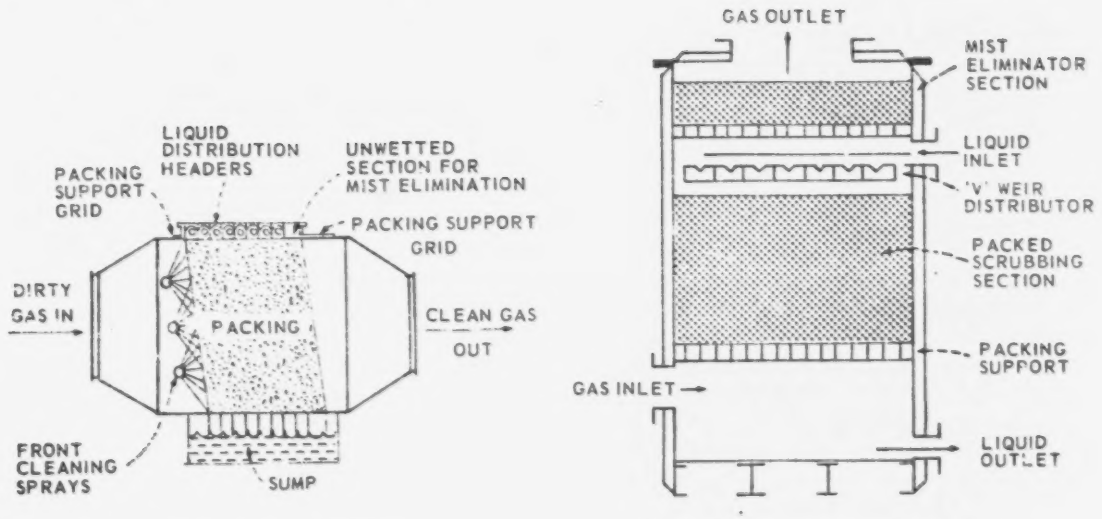

Figure 25. Typical packed bed scrubber units.

Source: US Department of Health, Education and Welfare. 1969. Control techniques for particulate air pollutants. National Air Pollution Control Administration, Washington DC, 215 p.

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effective absorbers; however, they do have some problems in handling gases containing particulates or contaminants that form precipitates or reactants within the packing media (Hill 1976).

- Spray Tower Scrubber

  Spray towers provide the interphase contacting necessary for gas absorption by dispersing the scrubbing liquid in the gas phase in the form of a fine spray. A typical layout for a spray tower is illustrated in Figure 26. Scrubbing liquid is sprayed into the gas stream and droplets fall by gravity through an upward flow of gas. The spray tower scrubber has the advantages of a very low pressure drop and an inexpensive construction cost but entrainment of scrubbing mists in the gas flow stream is a problem (USEPA 1977d).

- Spray-Crossflow Packed Bed Scrubber

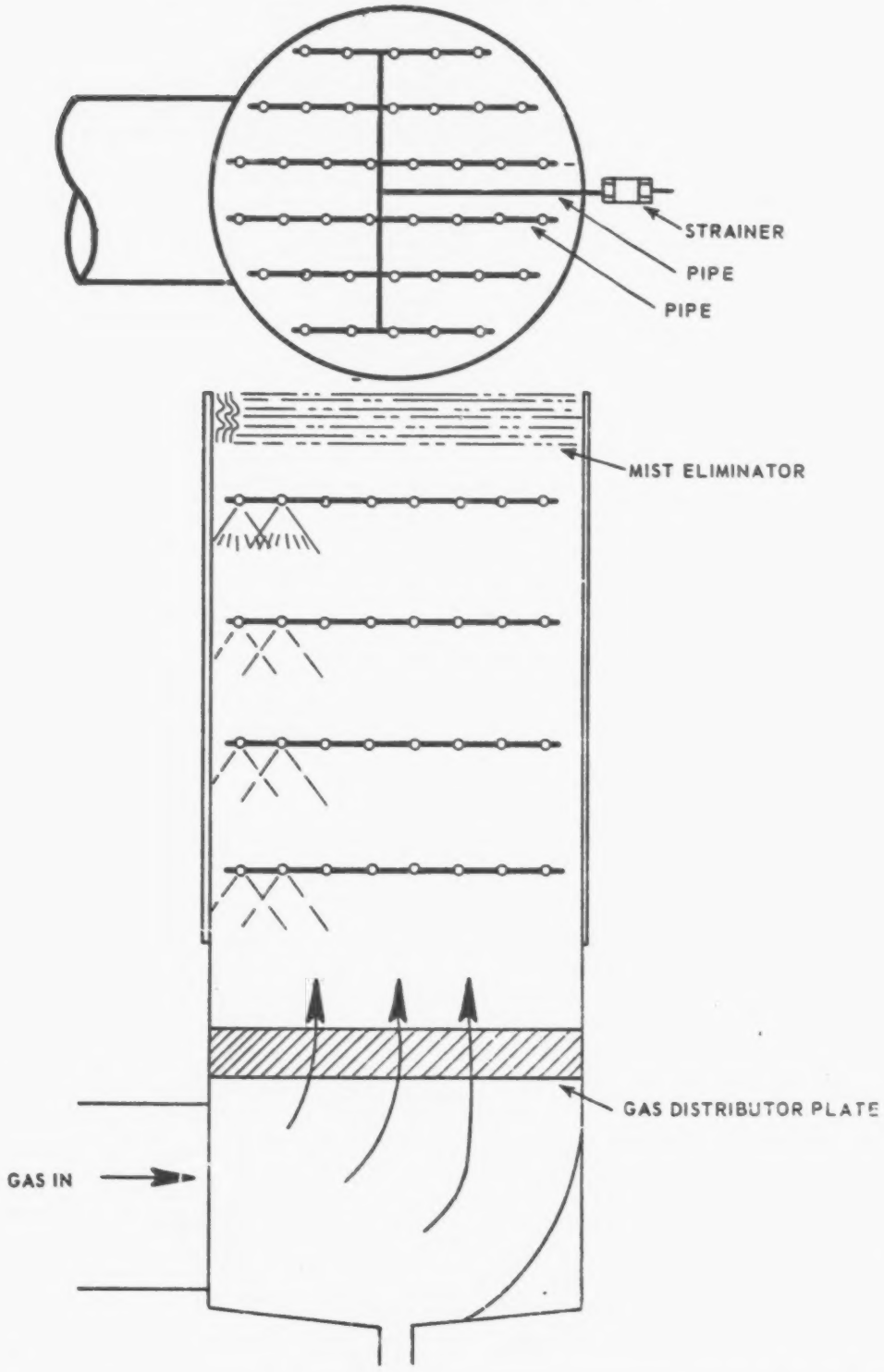
  The spray-crossflow packed bed scrubber has been accepted for several years by the fertilizer industry as the most satisfactory fluoride control device available for wet process phosphoric acid plants (USEPA 1977d). This spray-crossflow packed bed scrubber consists of a spray chamber and a packed bed separated by a series of irrigated baffles. All internal parts of the scrubber are constructed of corrosion resistant plastics or rubber-lined steel. General maintenance consists of replacement of the packing once or twice a year. Both the spray and the packed sections are equipped with a gas inlet. Effluent streams with relatively high fluoride concentrations (particularly those rich in silicon tetrafluoride) are treated in the spray chamber before entering the packing. This preliminary scrubbing removes silicon tetrafluoride, thereby reducing the danger of plugging the bed. At the same time, it reduces the loading on the packed stage and provides some solids handling capacity. Gases low in silicon tetrafluoride can be introduced directly to the packed section (USEPA 1977d). These systems may be found to be applicable to the significant fluoride emission control problems of the defluorinated phosphate rock and phosphorus production subcategories.

The effectiveness of a proposed control technique for a specific new source facility must be documented, to include:

- Sources that will be controlled.
- Effectiveness of collection devices.
- Removal efficiency of control devices.

The applicant should address the specific nature of all emissions to identify specific compounds that could be hazardous. These should be compared to the pollutants and standards currently established by the National Emissions

Figure 26. Typical layout for spray tower.



Source: US Department of Health, Education, and Welfare. 1969. Control techniques for participate air pollutants. National Air Pollution Control Administration, Washington DC, 215 p.

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Standards for Hazardous Air Pollutants (NESHAP). As of November 1979, the NESHAP program had established standards for these pollutants: asbestos, beryllium, mercury, and vinyl chloride (USEPA 1979c). These emissions normally are not associated with the non-fertilizer phosphate industry, but the applicant must confirm this for the specific new source.

3.2 STANDARDS OF PERFORMANCE TECHNOLOGY: WASTEWATER DISCHARGES

For most new sources in the phosphate industry, NSPS will require no discharge of process waste. To achieve this standard requires the conscious design of the entire plant to recycle, reuse, and reduce the use of water at every possible point. The EID should describe the integrated state-of-the-art production/treatment system designed to achieve the no-discharge goal. A detailed water balance should be developed showing the average and maximum flow rates expected for all wastewater streams.

3.2.1 In-Process Controls

In-process controls are procedures to reduce pollution discharges at their source, some of which result in product or by-product recovery, water conservation, energy conservation, and greater production efficiency. Those controls which are generally applicable include:

- Waste stream segregation.
- Water recycle and reuse.
- Reduction in water usage.
- Reduction of spill and runoff borne pollutants.
- Waste stream monitoring.

The application of in-process pollution controls to the wastewater streams of the industry are indicated in the following discussions.

3.2.1.1 Waste Stream Segregation

Because concentrated waste streams are more economically and efficiently treated than are large, dilute waste streams, it is advantageous to keep large volume but uncontaminated streams (such as cooling water) segregated from contaminated streams which could cause the entire combined stream to require treatment. A typical, generalized waste stream segregation scheme separates the following four streams.

- Non-contact, uncontaminated cooling water.
- Contaminated process water.
- Contaminated auxiliary process streams.
- Plant sanitary waste.

The uncontaminated cooling water stream may be reused or discharged with little or no treatment while the contaminated streams may be treated for product recovery, by-product recovery, reuse, or discharge.

For the defluorinated rock and phosphoric acid segments of the industry, cooling water, contaminated scrubber water, and contaminated runoff are not segregated but collected in a common pond system for neutralization, cooling, and solids separation. The quantity of water required for wet scrubbing is withdrawn from the pond, treated, and returned to the plant for use. Cooling water, which may not require treatment, is returned to the plant as needed.

3.2.1.2 Water Recycle and Reuse

Recycle and reuse are widely practiced in-process controls throughout the industry. The most commonly reused waste streams include cooling water, scrubber water, phosphorus seal (phossy) water, and quenching water. Process related streams commonly must be treated before reuse but these treatment practices do not result in waste discharges. The technologies available for this treatment of recycle streams are discussed in the wastewater treatment section.

3.2.1.3 Water Reduction

A considerable savings in wastewater generation can be effected by the use of dry dust collection devices such as cyclones and baghouses rather than wet scrubbers. Useable product may be recovered while reducing an intermedia transfer of waste. Plant cleanup practices also may be designed to maximize water savings. For example, reactor washdown using fine spray rather than high pressure fire hoses will save water and reduce the volume of cleanup wastes generated.

3.2.1.4 Reduction of Spill and Runoff

The use of bulk raw materials and production of finely divided dry bulk products by the industry makes site runoff a potentially significant source of contaminated water. Fugitive raw material and product dust coating the plant site can be transported by runoff to nearby waters. Leaks, spills, and process upsets which are not properly contained also can contribute to the runoff problem. Control of these pollution sources requires good housecleaning practices, maintenance, and containment. The EID should identify a positive plan for housecleaning to reduce the potential for contamination of runoff. Provisions should be made in plant design for containment and treatment of spills. Techniques for spill prevention and containment include:

- Use of corrosion resistant materials where needed.
- Regular repair and replacement of worn valves and pipes.
- Drip pans, canals, or sumps under process equipment.
- Dikes or containment vessels around reactors and storage vessels.
- Routing of plant runoff to the recycle containment pond.

3.2.1.5 Waste Stream Monitoring

Efficient and continuous monitoring is necessary to assure that accidents are detected and that pollutants are segregated into the proper waste management stream. Common techniques include:

- In-line continuous monitoring of spent stream flow rates and pH to warn operators of contamination and possible accidental discharge.
- Monitoring of selected streams for phosphorus, fluorine, total dissolved solids and suspended solids to identify long-term buildup of pollutants and the potential need for water system blowdown and discharge.

3.2.2 Wastewater Treatment

No discharge of process wastewater is allowed for most of the industry, so much of the wastewater treatment technology is directed toward recycle and reuse. Because a limited number of pollutants and problems characterize the waste from the industry, treatment technologies tend to be similar for most subcategories. This is illustrated in the control technologies described below. Wastewater treatment technologies described in the EID should include the source and nature of all wastewater in the plant, the processes for treatment of recycled process water, and any wastewater discharge (i.e., process wastewater, cooling water, runoff, or emergency discharge from the recycle pond). The treatment technologies described must be demonstrated as capable of meeting the stringent NSPS requirements for the industry.

3.2.2.1 Recycle of Wastewaters from the Defluorination of Phosphoric Acid, Defluorination of Phosphate Rock Subcategories

These subcategories have similar wastewater treatment problems and employ similar technologies. Wet scrubbers for control of emissions from defluorination of phosphate rock and phosphoric acid introduce large quantities of fluorine and phosphorus compounds into the wastewater stream. Wet emission control devices serving virtually all of the major processes for these industries also introduce highly acidic mineral wastes into the wastewater stream. To meet the stringent no-discharge requirements of NSPS, these process waste streams must be treated to the degree necessary to make the water acceptable for reuse or recycle. The acids must be neutralized, equipment fouling minerals removed, and suspended solids settled. The standard techniques for treating these wastewaters are lime treatment and use of recirculation (settling) ponds, which perform the following functions:

- Neutralization of acid waste waters.
- Sedimentation of much of the original suspended solids in the waste waters (silica, iron oxide, and others).
- Precipitation and sedimentation of much of the phosphates, fluorides, and sulfates which were dissolved in the original wastewaters.
- Dissipation of the process heat to the atmosphere during the extended residence in the settling ponds.
- Reduction in the wastewater quantity as a result of net evaporation during the extended residence in the settling ponds.
- Where phossy water is combined with these other process waters, some oxidation of the elemental phosphorus to phosphates is accomplished.

The limitations of these systems are that the ponds can overflow during excessively wet periods, and long detention times are required to remove the lighter precipitates (e.g., lime precipitated phosphates). Mechanical clarifier systems can be used, but these require that large volumes of light, poorly dewatering phosphorus sludge must be filtered mechanically and disposed on a regular basis (USEPA 1976a).

3.2.2.2 Recycle of Scrubber Wastewaters from the Phosphorus Production Subcategory

Similar technologies to those used by the defluorinated rock and acid producers are employed for wastewater treatment and recycle by the phosphorus production subcategory (although the ponds tend to be smaller). Highly acidic scrubber wastewater contaminated with fluorine and phosphorus compounds is routed to a recycle pond or tank where it is held for cooling and treatment. Lime is added either to the pond or to a portion of the water as it is bled off to a mechanical clarifier. Lime addition reduces the pH and precipitates out mineral contaminants in the form of calcium salts (calcium fluorides, calcium phosphate, calcium sulfates, etc.).

3.2.2.3 Recycle and Treatment of Phossy Water from the Phosphorus Producing and Consuming Subcategories

Phossy water from the phosphorus condenser and phosphorus air seals causes one of the industry's most dangerous and difficult waste management problems. Phossy water always is recycled although it must be treated to reduce the build-up of other undesirable dissolved solids. A portion of the colloidal phosphorus may be flocculated and settled in a clarifier with the effluent returned to the condenser or seals. Clarified effluent is then limed to precipitate the phosphorus and fluorides and returned to the plant (USEPA 1973a). The underflow from the clarifier containing 25% solids by weight can be treated by heating and distillation to recover the phosphorus. Wastewater from the phosphorus recovery process can be recycled to the phossy water pond (USEPA 1977c).

3.2.2.4 Treatment and Recycle of Process Water from Production of Anhydrous Phosphorus Derivatives

Phosphorus Pentoxide

The single raw waste constituent is phosphoric acid from water tail gas seals. Application of two standard techniques enables total recycle of this wastewater (USEPA 1973a):

- Reduction in wastewater quantities by using dilute caustic or lime slurry as tail gas liquor rather than pure water, increasing the absorptive capacity for P_2O_5.
- Lime treatment and sedimentation to neutralize and remove the phosphate, permitting total recycle.

Phosphorus Pentasulfide

The sole source of process wastewater is the scrubber liquor for fumes from casting liquid P_2S_5. One control technique would be the use of inert-atmosphere casting or vacuum casting to completely eliminate the need for

scrubbing. As an alternate to this approach, the application of three standard techniques would permit total recycle of scrubber water (USEPA 1973a):

- Use of dilute caustic or lime slurry rather than pure water would reduce the wastewater quantities by increasing the adsorptive capacity for P_2S_5 and SO_2.
- Both P_2S_5 and SO_2 are weakly absorbed by water and high flowrates are required to control these emssions.
- Partial recycle of scrubber liquor from a sump would reduce the wastewater quantity.
- Lime treatment and sedimentation to neutralize and remove phosphate, sulfite, and sulfate would permit total recycle.

Phosphorus Trichloride and Phosphorus Oxychloride

The treatment problem which makes reuse difficult for these processes is the difficulty of removing chlorides from the wastewater. Because chlorides are not precipitated with lime, they build up in the process water when recycled and require blowdown. Chlorides can be removed by reverse osmosis or prevented from building up in the scrubber water by condensing product vapors back into the product line before they reach the scrubber. The use of refrigerated condensers for emission control is described in Section 3.1. By rigorously reducing wastewater from other sources such as tank washing, the small amount of contaminated wastewater can be evaporated and the residue disposed of with other solid waste (USEPA 1973a).

3.2.2.5 Wastewater Treatment and Reduction in the Phosphate Chemicals Subcategory

Sodium Tripolyphosphate

All wastewater generated by production of STPP with dry process phosphoric acid is from wet scrubbing of dust from product drying operations. This wastewater may be reused in the neutralization step or as scrubber water after treatment. The use of dry emission control techniques such as baghouses could eliminate much of the process's water requirement (USEPA 1973a).

Calcium Phosphates

Wastewater from the production of animal and human food grade calcium phosphates result from wet scrubbing of dryer emissions and, in the case of human food grade dicalcium phosphate, filtrate from the reaction slurry. Complete recycle of the filtrate may be achieved by precipitation and vacuum filtration of the slurry and disposal of the filter cake. Wet scrubbers may be replaced by baghouses to eliminate the scrubber wastewater at its source (USEPA 1973a).

3.2.2.6 Sodium Wastewater Treatment for Production of Phosphates from "Wet Process" Phosphoric Acid

The rather complicated process of manufacturing purified sodium phosphates from "wet process" phosphoric acid produces wastewater from filtration washes, gas scrubber liquors, and leaks and spills. Periodic slugs of contaminated site runoff also contribute to the wastewater load. Similar to the rest of the industry, the heart of the wastewater treatment system for this process is also a recirculation/treatment pond; however, the use of significant quantities of water in the manufacturing process and the lack of large water losses from cooling make the discharge of some wastewater a necessity. The recommended treatment technology for this discharge is the double liming process described in Section 3.2.3 for emergency discharge of recirculation pond effluent.

3.2.3 Emergency Discharge of Recirculation Pond Effluent

The contaminated water stored in the recirculation pond must be treated prior to any discharge necessitated by unusually high rainfall (which should be in excess of the local 24-hour, 25-year frequency event). Once the storage area approaches capacity it is necessary to begin treating the contaminated water for subsequent discharge to natural drainage bodies.

Treatment must accomplish NSPS levels for phosphorus, fluorides, and total suspended solids (TSS). In most cases pH also is regulated by means of the NPDES permit. "Double liming," or a two stage lime neutralization, is the

standard of performance control technology for the fertilizer industry and is also applicable to wastewater streams from large volume recycle systems in the non-fertilizer phosphate industry (USEPA 1976a).

The first treatment stage provides sufficient chemical addition to increase the pH of the contaminated water (containing up to 9,000 mg/l F and up to 6,500 mg/l P) from the range of pH 1-2 to pH 3.5-4.0. The resultant treatment effectiveness largely is dependent on constancy of the pH control. At a pH of 3.5 to 4.0, the fluorides will precipitate principally as calcium fluoride (CaF_2). This mixture is held in a quiescent area to allow the particulate CaF_2 to settle.

Equipment used for neutralization ranges from crude manual distribution of lime with localized agitation to a well engineered lime control system with a compartmented mixer. The quiescent areas may range from a pond to a controlled settling rate thickener or settler. The partially neutralized water (pH 3.0-3.5) after separation from the CaF_2 should contain about 30-60 mg/l F and up to 5,500 mg/l P. This water is again treated with lime to increase the pH to 6.0 or above. At this pH level calcium compounds (primarily calcium phosphates ($CaHPO_4$) plus additional quantities of CaF_2), precipitate from solution. As before, this mixture is retained in a quiescent area to allow the $CaHPO_4$ and minor amounts of CaF_2 to settle.

The removal of phosphorus is strongly dependent upon the final pH level, holding time, and quality of the neutralization facilities, particularly the mixing efficiency. Figure 27 shows a sketch of a well designed "double lime" treatment facility for a fertilizer plant gypsum pond. The same technology is applicable to treatment of defluorinated phosphate rock or acid recirculation pond overflows.

3.2.4 Recirculation Pond Water Seepage Control

The contaminated water storage areas (recirculation pond) are surrounded by dikes except when mining pits are used. The base of these dikes is normally natural soil from the immediate surroundings. When height of the retaining dikes must be increased in the phosphate fertilizer industry, gypsum from

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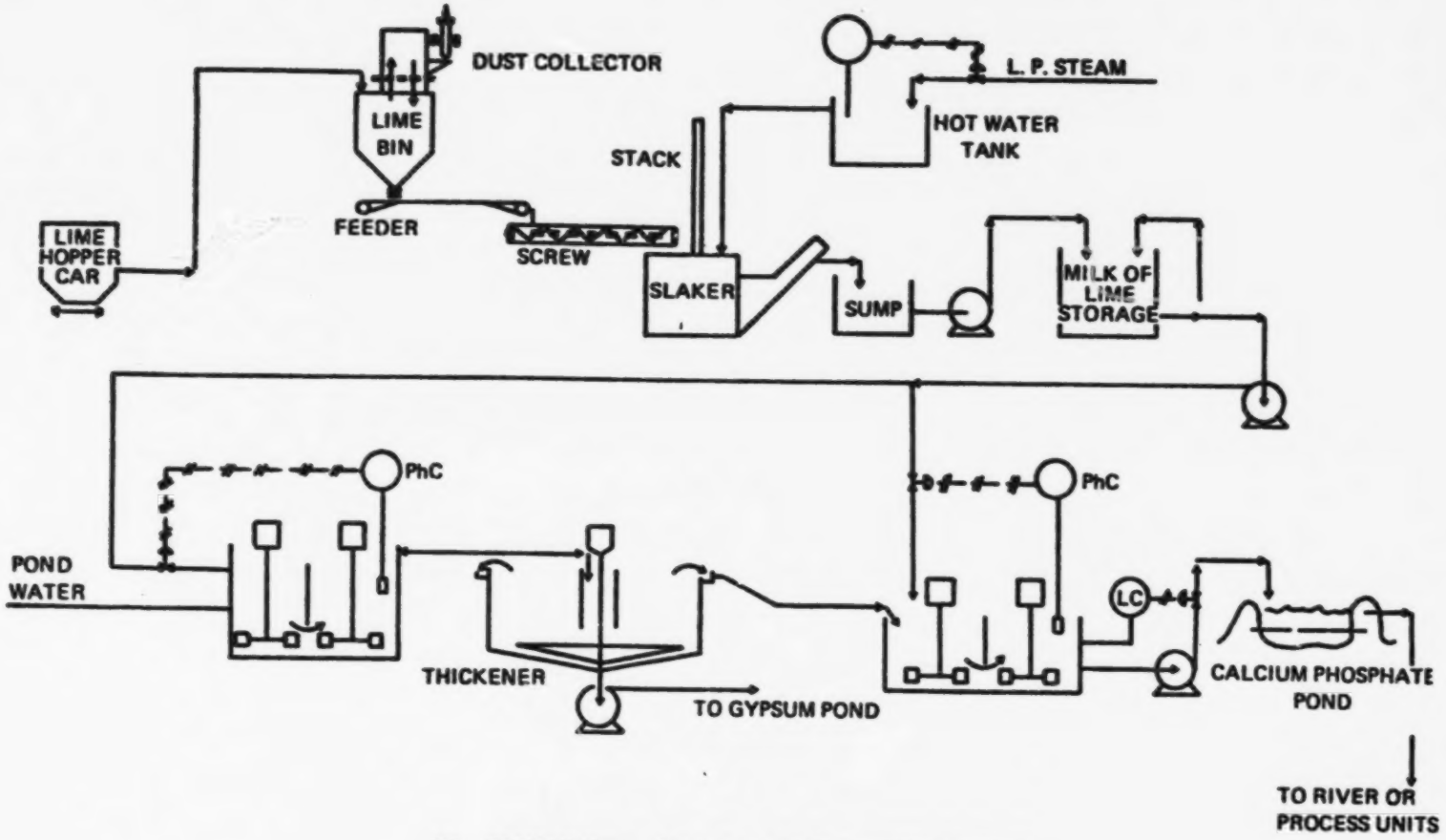

CC TAMINATED (POND) WATER TREATMENT

Figure 27. Pond water treatment system.

Source: US Environmental Protection Agency. 1974a. Development document for effluent limitations guidelines and new source perfcrmance standards for the basic fertilizer chemicals segment of the fertilizer manufacturing point source category. Office of Air and Water Programs, Washington DC, 168p.

inside the diked area is added to the top of the earthen base. Dikes in Florida now extend 100-120 ft in vertical height and tend to have continual seepage of contaminated water through them. The extent of this problem in the non-fertilizer phosphate industry is not known but industry similarities make seepage a possibility. To prevent pond seepage from reaching natural drainage streams, it should be collected and returned to the pond.

Figures 28 and 29 illustrate the design and use of a seepage collection ditch around the perimeter of the diked area. The ditch should be of sufficient depth and size to collect contaminated water seepage and to permit collection of seepage surface water from the immediate outer perimeter. This is accomplished by erection of a small secondary dike. The secondary dike also serves as a back-up or reserve dike in the event of a failure of the major dike. The installation of a pump station at the collection point of the seepage ditch is an essential part of the control system.

3.3 STATE OF THE ART TECHNOLOGY: SOLID WASTE

Solid waste control technologies practiced by the non-fertilizer phosphate industry include:

- Recovery and reuse.
- Pond storage.
- Landfilling.

Tables 25, 26 and 27 indicate solid waste management technologies that could be used by manufacturers in the various subcategories.

3.3.1 Recovery and Reuse

Raw material and product recovery are significant solid waste management strategies in this industry. The use of dry bulk raw materials and the production of many fine-grained dry products provide opportunities for recovery of valuable materials that would otherwise be wasted as dust. Recovery of elemental phosphorus from phossy water is a necessity since this toxic, highly

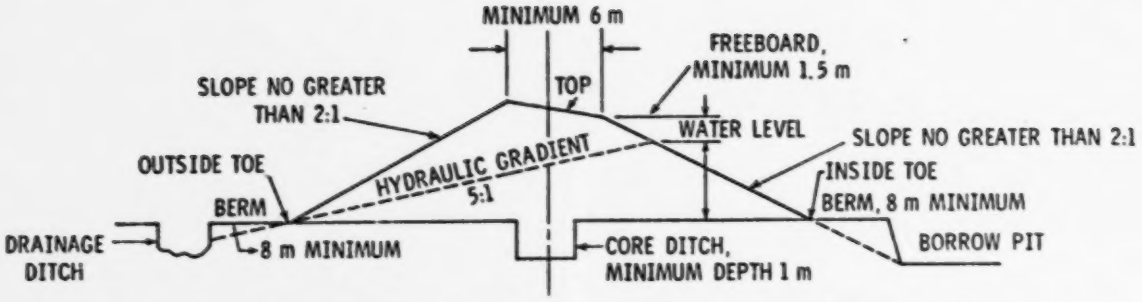

Figure 28. Recommended minimum cross section of dam.

Reprinted from Phosphoric Acid, Volume I, A.V. Slack, Editor, by permission of Marcel Dekker, Inc., Year of first publication 1968.

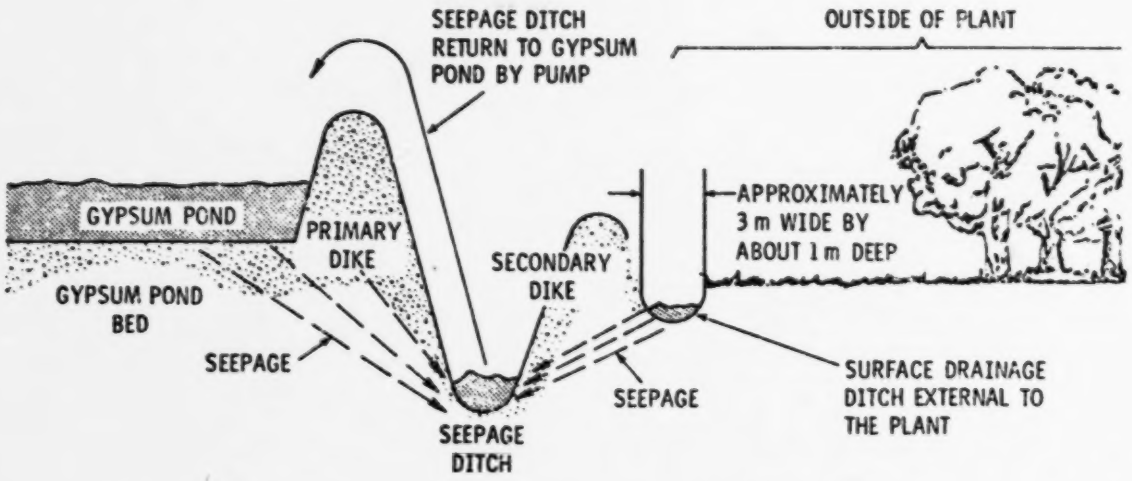

Figure 29. Gypsum pond water seepage control.

Source: Environmental Protection Agency. 1974a. Development document for effluent limitations guidelines and new source performance standards for the basic fertilizer chemicals segment of the fertilizer manufacturing point source category. Office of Air and Water Programs, Washington DC, 168 p.

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Table 25. Treatment and disposal technologies for process solid wastes of the phosphorus production subcategory.

Solid Waste	Contaminants	Treatment	Disposal
Furnace Slag	Fluorides, phosphates[1] metals, uranium	Cooling[2] detoxification	Land disposal and sale[3] for road bed construction
Scrubber Precipitates	Fluorides, phosphates Calcium floride	Liming, precipitation[2] evaporation asphalting	Pond storage or land disposal
Calciner precipitator dust	Phosphates	Recovery	-
Phosphorus condenser mud	Phosphorous	Recovery	-
Phossy water treatment solids	Phosphorous	Heat treatment and distillation	Pond storage or land disposal
Electrostatic precipitator dust	Phosphates fluorides	Recovery	-

[1] Hazardous waste, must be handled, transported and disposed of according to 40 CFR 261.

[2] Source: Abrams, E.F., G. Contos, and M. Drabkin, Versar-Inc. 1977. Alternatives for hazardous waste management in the inorganic chemicals industry. Prepared for the Office of Solid Waste, Hazardous Waste Management Division, US Environmental Protection Agency. Washington DC.

Source: Stinson, Mary K. and E.E. Berkan, Hazardous Waste Generation in the Inorganic Chemicals Industry." Paper presented at the National Conference on Hazardous and Toxic Waste Management, June 3-5, 1980, Newark, N.J.

[3] Source: US Environmental Protection Agency. 1973a. Development document for proposed effluent limitations guidelines and new source performance standards for the phosphorus derived chemicals segment of the phosphate manufacturing point source category. Office of Air and Water Programs, Washington DC, 159 p.

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Table 26. Treatment and disposal technologies for process solid wastes of the phosphorus consuming and calcium phosphates subcategories.

Solid Waste	Contaminants	Treatment	Disposal
P_2S_5 still residue	Arsenic pentasulfide phosphorus phosphorus sulfides	Butadiene encapsulation,[2]	Land disposal
P_2S_5 dust	Phosphorus phosphorus sulfides	Recycle	--
Phosphoric acid purification residue	Arsenic sulfides	Butadiene encapsulation,[1,2]	Land disposal
Phosphoric acid scrubber solution precipitates	Phosphorus, fluorides	Neutralization[2] precipitation	Pond or land disposal
Phosphorus trichloride still bottoms	Arsenic trichloride	1) distillation and[2] recovery 2) convert to less re-[1] active arsenic sulfides, encapsulation	-- Land disposal or by-product sales
Food grade calcium phosphates sweepings	Lime, phosphates		Land disposal

---

Unproven technologies: At the time at which these technologies were identified they had not been tested in the suggested application.

[1] Source: Abrams, E.F., G. Contos and M. Drabkin, Versar, Inc. 1977. Alternatives for hazardous waste management in the inorganic chemicals industry. Prepared for the Office of Solid Waste, Hazardous Waste Management Division, U.S. Environmental Protection Agency, Washington DC.

[2] Source: US Environmental Protection Agency. 1973a. Development document for proposed effluent limitations guidelines and new source performance standards for the phosphorus derived Air and Water Programs, Washington DC, 159 p.

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Table 27. Treatment and disposal technologies for process solid wastes from the defluorinated phosphate rock, defluorinated phosphoric acid, and sodium phosphates subcategories.

Solid Waste	Contaminants	Treatment	Disposal
Defluorination of phosphate rock			
Calciner dust	Phosphates, fluorides	Recycle	--
Wet scrubber precipitates	Calcium fluorides, sulfates, and phosphates	Lime precipitation	Pond storage
Defluorination of phosphoric acid			
Wet scrubber precipitates	Calcium fluorides, sulfates and phosphates	Lime precipitation	Pond storage
Sodium phosphates			
Raw material and product dust	Phosphates	Reclaim	-
Sodium fluosilicate	Sodium fluosilicate	-	By-product sales
Arsenic sludge	Arsenic sulfate	Encapsulation	Land disposal
Process sludge	Iron, aluminum, phosphates, fluoride	Dewatering	By-product sales

Source: US Environmental Protection Agency. 1976a. Development document for effluent limitations guidelines and new source performance standards for the other non-fertilizer phosphate segment of the phosphate manufacturing point source category. Office of Water and Hazardous Materials, Washington DC, 105 p.

reactive material cannot be allowed to come into contact with air. Some of the more toxic, small volume wastes of the industry such as arsenic trichloride have now become profitable to recover (Abrams et al. 1977). This type of solid waste management is encouraged and should be fully explored in the EID.

3.3.2 Solid Waste Storage and Disposal

The largest volume of industry solid waste derives from precipitates from the treatment of emission control scrubber water. These solids are collected in a cooling/recirculation pond or dewatered and hauled to a landfill. Although lime precipitated solids are largely insoluble, they may be toxic--as in the case of calcium fluorides--and should be tested for potential leaching and resultant contamination of groundwater. Other non-hazardous, solid plant wastes including calcium phosphate sweepings and general trash may be landfilled without difficulty.

3.3.3 Hazardous Wastes

Wastes such as electric furnace slag that are classified as hazardous according to RCRA will require special handling and tracking as specified in 40 CFR Parts 264 and 265. The regulations urge that where practical, alternatives to disposal such as treatment, recovery, or destruction be considered. The EID should identify the alternative means of hazardous waste management evaluated in the project planning and demonstrate why the selected technology was chosen. The chosen technology should be presented in detail showing how much waste is to be generated, how it is to be handled, and its final disposition. If final disposal in a hazardous waste disposal site is chosen, the EID should identify the means of transportation to the site, the suitability of the site to accept the waste, and its capacity to accept the waste.

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4.0 EVALUATION OF AVAILABLE ALTERNATIVES

The alternatives section of the EID should address each reasonable alternative available for the new source phosphate facility. The purpose of this analysis is to identify and evaluate alternate plans and actions that may accomplish the desired goals of the project. These alternatives can include process modifications, site relocations, project phasing, or project cancellation.

For the alternatives to a proposed project to be identified and evaluated properly, the impact assessment process should commence early in the planning phase. In this manner, social, economic, and environmental factors against which each alternative is to be judged can be established. Cost/benefit analysis should not be the only means whereby alternatives are compared; the environmental and social benefits of each alternative also must be considered. In general, the complexity of the alternative analyses should be a function of the magnitude and significance of the expected impacts of the proposed processing operations. A small processing facility located in an area with an established industry of the same kind may have a relatively minimal impact on a region and generally would require fewer alternatives to be presented in the EID.

The public's attitude toward the proposed operation and its alternatives also should be evaluated carefully. In this way key factors such as aesthetics, community values, and land use can be assessed properly.

4.1 SITE ALTERNATIVES

As with all industries, the non-fertilizer phosphate industry locates plants on the basis of several factors:

- Market demand for its products.
- Convenience to raw materials.
- Availability of an adequate labor force and water supply.

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- Proximity to energy supplies and transportation.
- Minimization of environmental problems.

A variety of sites initially should be considered by the applicant. The EID should contain an analysis of each one, with the preferred alternative selected on the basis of satisfying the project objectives with the least adverse environmental impact.

Consultation with the appropriate resource agencies during the early stages of site selection is recommended. Key agencies that can provide valuable technical assistance include:

- State, Regional, County, or Local Zoning or Planning Commissions. These sources can describe land use programs and determine if variances would be required. Federal lands are under the authority of the appropriate Federal land management agency (Bureau of Reclamation, US Forest Service, National Park Service, etc.).
- State or Regional Water Resource Agencies. These sources can provide information relative to water appropriations and water rights.
- Air Pollution Control Agencies. These sources can provide assistance relative to air quality increments and other air-related standards and regulations.
- The Soil Conservation Service and State Geological Surveys. These sources can provide data and consultation on soil conditions and geologic characteristics.

Further consideration should be given to any state siting laws. The applicable regulations should be cited and any applicable constraints described.

The EID should include the potential site locations on maps, charts, or diagrams that show the relevant site information. (A consistent identification system for the alternative sites should be established and retained on all graphic and text material.) These should display pertinent information that includes, but is not limited to:

- Areas and sites considered by the applicant.
- Major centers of population density (urban, high, medium, low density, or similar scale).

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- Waterbodies suitable for cooling water or effluent disposal.
- Railways, highways (existing and planned), and waterways suitable for the transportation of materials.
- Important topographic features (such as mountains and marshes).
- Dedicated land use areas (parks, historic sites, wilderness areas, testing grounds, airports, etc.).
- Other sensitive environmental areas.

Using the foregoing graphic materials, the applicant should provide a condensed description of the major considerations that led to the selection of the final candidate areas, including:

- Proximity to markets and raw materials.
- Economic analyses with trade-offs.
- Adequacy of transportation systems.
- Environmental aspects, including the likelihood of floods.
- License or permit problems.
- Compatibility with existing land use planning programs.
- Current attitudes of interested citizens.

The EID should indicate the steps, factors, and criteria used to select the proposed site. Quantification, although desirable, may not be possible for all factors because of lack of adequate data. Under such circumstances, qualitative and general comparative statements supported by documentation may be used. Where possible, experience derived from operation of other plants at the same site or at an environmentally similar site may be helpful in appraising the nature of expected environmental impacts.

The factors considered in selecting each site, and especially those that influenced a positive or negative decision on its suitability, should be carefully documented in the permit applicant's EID. Adequate information on the feasible alternatives to the proposed site is a necessary consideration in issuing, conditioning, or denying an NPDES permit. Specifically, the ad-

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vantages and disadvantages of each alternative site must be catalogued with due regard to preserving natural features such as wetlands and other sensitive ecosystems and to minimizing significant adverse environmental impacts. The applicant should ascertain that all impacts are evaluated as to their significance, magnitude, frequency of occurrence, cumulative effects, reversibility, secondary or induced effects, and duration. Accidents or spills of hazardous or toxic substances vis-a-vis site location should be addressed.

A proposed site may be controversial for a number of reasons:

- Impact on a unique, recreational, archaeological, or other important natural or man-made resource area.
- Destruction of the rural or pristine character of an area.
- Conflict with the planned development for the area.
- Opposition by citizen groups.
- Unfavorable meteorological and climatological characteristics.
- Periodic flooding, hurricanes, earthquakes, or other natural disasters.

If the proposed site location proves undesirable, then alternative sites from among those originally considered would be reevaluated, or new sites should be identified and evaluated. Expansion at an existing site also could be a possible alternative solution. Therefore, it is critical that a permit applicant systematically identify and assess all feasible alternative site locations as early in the planning process as possible.

4.2 ALTERNATIVE PROCESSES AND DESIGNS

Typically the analysis of alternative processes and designs for a new industrial facility are already complete and a design selected before an EID is prepared. This selection process is primarily an economic one but it is usually carried out in full awareness of environmental and energy constraints. However, the industry should evaluate all feasible alternatives to ensure that the most cost-effective and environmentally sound alternative is selected.

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Process selection is geared to maximizing production at the minimum cost. For small operations with only an area or regional market this may be quite different than for a plant designed for a large national or international market. Within these production ranges the same economic concerns must be dealt with, however. The rising cost of energy may push producers of calcium and sodium phosphates toward the use of purified wet acid as a raw material rather than "dry process" acid from energy intensive elemental phosphorus. The cost of emission controls and energy may indicate that a chemical/aeration method for defluorinating phosphoric acid is more favorable than the vacuum condensation method. The EID should indicate the criteria and methodology used to develop, screen, and select the processes and design of the new source phosphate facility and justify the selection over others that may be more advantageous in other respects.

4.2.1 Process Alternatives

Process alternatives are usually selected on the basis of the following:

- Product demand.
- Reliability of the process.
- Engineering feasibility.
- Economics.
- Availability of required raw materials.
- Environmental considerations.

Those alternatives that appear practical should be considered further on the basis of criteria such as:

- Land requirements of the processing facility, fuel storage facilities, waste storage facilities, and exclusion areas.
- Release to air of dust, sulfur dioxide, nitrogen oxides, and other potential pollutants subject to Federal, state, or local limitations.
- Releases to water of heat and chemicals subject to Federal, state, and local regulations.

- Effectiveness of pollution abatement technology.
- Water consumption rate.
- Energy consumption.
- Social impacts of increased traffic as materials are transported to the site and wastes and products are transported from the site.
- Social effects resulting from the influx of construction, operation, and maintenance crews.
- Economics.
- Aesthetic considerations for each alternative process.
- Reliability and energy efficiency.

A tabular or matrix form of display often is helpful in comparing the feasible alternatives. The EID should present clearly and systematically the methodology used to identify, evaluate, and select the preferred process alternative. Alternative processes which are not feasible should be dismissed with an objective explanation of the reasons for rejection.

4.2.2 Design Alternatives

In order to properly present alternative facility designs available for the project in the EID, the combination of component systems available for selection should be analyzed and described for the following factors:

- Capital and operating costs.
- Environmental considerations.
- System reliability and safety.

All of these factors should be documented and quantified wherever possible.

4.3 NO-BUILD ALTERNATIVE

In all proposals for industrial development, the alternative of not constructing the proposed new source facility must be considered. This analysis is not unique to the development of phosphate manufacturing facilities (see

Chapter IV, Alternatives to the Proposed New Source, in the USEPA document, Environmental Impact Assessment Guidelines for Selected New Sources Industries, October 1975). The key aspects of the no-build alternative should be identified to include:

- Market Effect. Not constructing the facility may result in product shortages.
- Industry Effect. Not constructing the facility may cause dated facilities to be renovated.
- Technology Effect. Not constructing the facility may delay the need for expanded capacity, which may allow time for improved technology to be incorporated into the facility.
- Environmental Effect. Not building the facility might avoid adverse environmental effects at the proposed site, but subsequently may cause similar effects at a more sensitive site.

Other factors should be considered (e.g., specific environmental issues) as appropriate for the situation leading to the proposed action.

5.0 REFERENCES

The literature references in this section include cited references and additional bibliographic references. The listings immediately below are short form citations arranged according to topics. A complete listing of full references, arranged alphabetically, follows the short form citations.

5.1 REFERENCE LIST BY TOPIC

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16. ABSTRACT

This guideline document has been prepared to augment the information previously released by the Office of Federal Activities entitled Environmental Impact Assessment Guidelines for Selected New Source Industries. Its purpose is to provide guidance for the preparation and/or review of environmental documents (Environmental Information Document or Environmental Impact Statement) which EPA may require under the authority of the National Environmental Policy Act (NEPA) as part of the new source (NPDES) permit application review process.

This document has been prepared in six sections; organized in a manner to facilitate analysis of the various facets of the environmental review process. The initial section includes a broad overview of the industry intended to familiarize the audience with the processes, trends, impacts and applicable pollution regulations commonly encountered in the non-fertilizer phosphate industry. Succeeding sections provide a comprehensive identification and analysis of potential environmental impacts, pollution control technologies available to meet Federal standards, and other controlable impacts. The document concludes with two sections: available alternatives, and a comprehensive listing of references for further reading.

17. KEY WORDS AND DOCUMENT ANALYSIS

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